PB-232 012

EVALUATION OF THE REGENERATIVE PRESSURIZED FLUIDIZED-BED COMBUSTION PROCESS

M. W. Kellogg Company

PREPARED FOR
Environmental Protection Agency

February 1974

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1. REPORT NO.	2.	3. PB 232 012
EPA-650/2-74-012		

4. TITLE AND SUBTITLE	5. REPORT DATE
Evaluation of the Regenerative Pressurized Fluidized-Bed Combustion Process	February 1974
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) T. E. Johnson, A. G. Sliger, P. A. Lefrancois, and D. O. Moore	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS M. W. Kellogg Company 1300 Three Greenway Plaza East Houston, Texas 77046	10. PROGRAM ELEMENT NO. 1AB013, ROAP 21ADE-10
	11. CONTRACT/GRANT NO. CPA 70-68 (Task 9)
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development NERC-RTP, Control Systems Laboratory Research Triangle Park, N.C. 27711	13. TYPE OF REPORT AND PERIOD COVERED Final
	14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT The report gives results of an in-depth literature search into the regeneration chemistry of $CaSO_4$ and $CaSO_4 \cdot MgO$. It presents an evaluation of this chemistry and recommendations for potential processing schemes. Included are process flow sheets, material balances, process descriptions, and solids handling techniques for one- and two-step regeneration. It delineates areas where additional experimental data are needed to confirm assumptions. Esso Research and Engineering has conducted extensive studies toward developing a regenerative pressurized fluidized limestone bed coal combustion process using either limestone or dolomite as the SO_2 acceptor. This process requires a regeneration step to convert the sulfated acceptor back to lime for recycle to the combustor.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Fluidized-Bed Processing	Air Pollution Control	13B
Reviewing	Regeneration (Engineering)	Stationary Sources	17B
Evaluation	Pressurizing	Regenerative, Pressurized Fluidized-Bed Combustion	14A
Coal	Limestone		
Combustion	Dolomite (Rock)		
Desulfurization			

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Unlimited		102
	20. SECURITY CLASS (This page)	22. PRICE $4.50

EPA Form 2220-1 (9-73)

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EPA-650/2-74-012

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Contract No. CPA 70-68 (Task 9)
ROAP No. 21ADE-10
Program Element No. 1AB013

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Research Triangle Park, North Carolina 27711

Prepared for

OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

February 1974

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This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

TABLE OF CONTENTS

		PAGE NO.
I.	Introduction	1
II.	Summary and Conclusions	2
III.	Basis of Evaluation	4
IV.	Regeneration Chemistry	6
	A. 1-step Process B. 2-step process	
V.	Process Descriptions	7
	A. One-step regeneration process	7
	B. Two-step regeneration process	12
	C. Special Equipment for Sulfur Condensation	16
VI.	Discussion of Solids Handling	17
	A. One-step regeneration - low pressure case	17
	B. One-step regeneration - high pressure case	20
	C. Two-step regeneration	21
VII.	Process Design Notes	23
	A. Combustor Design Basis	23
	B. Regenerator Calculations	25
	C. Fluidized Vessel Calculations	26
	1. Minimum Fluidization Velocity 2. Slugging Height 3. Transport Disengaging Height 4. Solids Entrainment	
	D. H_2S Plant	29
	E. Sulfur Plant	30

TABLE OF CONTENTS (cont'd.)

	PAGE NO.
VIII. Process Appraisals	32
A. Comparison of the Processes	32
1. Utilities	
2. Solids Handling and Operability	
3. Processing Steps	
B. Areas Requiring Further Investigation	34
1. Fly Ash	
2. Lime Attrition	
3. Kinetics of Regeneration	
4. Elemental Sulfur in Regenerator Effluent	
5. Trace Elements	
IX. References	39
X. Appendices	40
A. Process Flow Sheet - One Step Process (Figure 1)	42
B. Process Flow Sheet - One Step Process - Sulfur Plant & H_2S Plant (Figure 2)	44
C. Stream Summaries - One Step Process (Table 1)	45
D. Process Flow Sheet - Two Step Process (Figure 3)	52
E. Process Flow Sheet - Two Step Process - Sulfur Plant (Figure 4)	54
F. Stream Summaries - Two Step Process (Table 2)	55
G. Solids Handling Diagrams (Figures 5, 6, 7)	60
H. Combustor Heat Balance (Table 3)	63
I. Equilibrium Yields - One Step Regeneration (Table 4)	64
J. Equilibrium Yields - Two Step Regeneration - 1st Stage (Table 5)	65
K. Equilibrium Yields - Two Step Regeneration - 2nd Stage (Table 6)	66
L. Combustor & Regenerator Dimensions & Design Parameters (Table 7)	67
M. Reduction of $CaSO_4$-Summary of Literature Search	68

LIST OF TABLES

TABLE NO.	DESCRIPTION	PAGE NO.
1	Stream Summaries - One Step Process	45
2	Stream Summaries - Two Step Process	55
3	Combustor Heat Balance	63
4	Equilibrium Yields for One Step Regeneration	64
5	Equilibrium Yields for Two Step Regeneration - 1st Stage	65
6	Equilibrium Yields for Two Step Regeneration - 2nd Stage	66
7	Combustor and Regenerator Dimensions and Design Parameters	67

LIST OF FIGURES

FIGURE NO.	DESCRIPTION	PAGE NO.
1	Process Flow Sheet - One Step Process	42
2	Process Flow Sheet - One Step Process - Sulfur Plant and H_2S Plant	44
3	Process Flow Sheet - Two Step Process	52
4	Process Flow Sheet - Two Step Process - Sulfur Plant	54
5	Solids Handling - One Step Process - Low Pressure Regeneration	60
6	Solids Handling - One Step Process - High Pressure Regeneration	61
7	Solids Handling - Two Step Process	62

I. Introduction

This report covers work performed under Contract No. CPA 70-68, Environmental Protection Agency, Office of Research and Monitoring. Task specifications were delineated by ORM in Task #9 contract specification request and supplemented later by letter following discussions between ORM and MWK based on results obtained in the first phase of the work.

The objective of this task was to provide data to supplement Esso Research and Engineering's work directed toward developing a continuously regenerable pressurized fluidized limestone bed combustor using either limestone or dolomite as the SO_2 acceptor.

The task, in short, specifies that an in-depth literature survey be conducted into the high pressure (~10 atmospheres) regeneration chemistry of $CaSO_4$ and $CaSO_4 \cdot MgO$ followed by an evaluation of this chemistry. In addition, recommendations on potential processing schemes were requested, as were suggestions for tasks necessary for further evaluation of these schemes.

The report is based primarily on the Interim Report (January 1, 1971-June 1, 1971) of Esso Research and Engineering Company(3)*. The Final Report from Esso issued in May, 1972, was not made available to M.W. Kellogg during the time the work was done.

*References included as Section IX of this report.

II. Summary and Conclusions

An extensive literature search was conducted for data on the reduction of $CaSO_4$ or $CaSO_4 \cdot MgO$ under pressure. Very little pertinent data were found for this reaction under pressure so analysis of the system was based on the literature and experience at atmospheric pressure. Feasibility of several key reactions have been established at 220 psia but kinetic data apparently have not been obtained; however, the pressure effect should be advantageous in most of the major reactions in question. (The results of the literature search are discussed in detail in the Appendix, Part M of this report).

Preliminary process designs consisting of flow sheets and heat and material balances have been prepared for the desulfurization of coal in a 15 MW fluidized bed boiler using the regenerable limestone concept. Data necessary for the designs have been taken from Esso Research and Engineering Company Interim Report January 1, 1971 - June 1, 1971, along with pertinent information taken from the literature. The emphasis of this study has been on investigating the viability of the lime regeneration schemes by demonstrating the sulfur recovery procedures and the solids handling techniques which could be used. Thus, it was assumed that the kinetics of the various reactions were feasible. No optimization of process design was made nor was any detailed equipment design done.

Two processes embodying different regeneration concepts have been developed:

- A 1-step regeneration process which operates at high temperatures and produces a concentrated SO_2 stream for further processing to elemental sulfur.
- A 2-step regeneration process which operates at relatively low temperatures and produces an H_2S stream for conversion to elemental sulfur.

With the exception of the regeneration reactors and the combustor, it has been found that the processes need to contain only commercially proven concepts and technology to be workable. From this standpoint then, the regenerable limestone/fluidized bed boiler concept provides the potential nucleus for a viable coal desulfurization process.

III. Basis of Evaluation

The following general overall design bases and parameters used in the process evaluation were mutually derived by ORM and MWK:

- The effort is limited to a technical feasibility study only; no cost estimates are included.
- A complete system is considered, all equipment and processing steps necessary for the production of elemental sulfur, with recycle of sulfur plant tail gas, is included.
- The plant size studied will be in the 10-20 MW range.
- Only pressurized operation of the fluid bed combustor is considered. The pressure used will coincide with Esso's pilot plant design, viz., 150 psig (10 atmospheres).
- A dolomitic limestone is used as the desulfurizing agent and about 10% fresh stone is added as makeup, basis stoichiometric requirements.
- Regeneration is evaluated for both pressurized (150 psig) and atmospheric operation.
- It is assumed that natural gas is available for the regeneration thereby eliminating the need for reducing gas production.
- Data needed for the evaluation are taken from an Esso report(3) supplemented by literature data as required.

Regeneration for the 1-step process at both 40 psia and 152 psia was considered with the result that the only important difference found between these two was in the ease of solids handling in the high pressure case. Only high pressure design was considered for the 2-step process since chemical equilibrium limitations existed at atmospheric pressure. Feasible solids handling circuits for both regeneration processes were developed.

A list of topics requiring further laboratory study for purposes of eventual process design has been prepared. Most important among the items requiring further development are:

- Details on the behavior of coal fly ash in the combustor
- Data on attrition of lime in the fluidized beds
- Data on the kinetics of the three regeneration reactions

IV. Regeneration Chemistry

The basic chemical reactions involved in the two regeneration processes which were considered are based on reduction of $CaSO_4$ with CO and H_2 at elevated temperatures:

A. 1-step process

$$CaSO_{4(s)} + \begin{bmatrix} CO \\ H_2 \end{bmatrix}_{(g)} \rightleftharpoons \begin{bmatrix} CO_2 \\ H_2O \end{bmatrix}_{(g)} + SO_{2(g)} + CaO_{(s)} \quad (1)$$

B. 2-step process

$$CaSO_{4(s)} + 4 \begin{bmatrix} CO \\ H_2 \end{bmatrix}_{(g)} \rightleftharpoons CaS_{(s)} + 4 \begin{bmatrix} CO_2 \\ H_2O \end{bmatrix}_{(g)} \quad (2)$$

$$CaS_{(g)} + H_2O_{(g)} + CO_{2(g)} \rightleftharpoons CaCO_{3(s)} + H_2S_{(g)} \quad (3)$$

$$CaCO_{3(g)} \rightleftharpoons CaO_{(g)} + CO_{2(g)} \quad (4)$$

Reaction (1) has been observed to proceed rapidly to equilibrium at temperatures of 2000°F and 1 atm pressure (1). Below 1800°F equilibrium favors reduction to CaS via reaction (2) although there are very little experimental data to back up the feasibility of this reaction. At a temperature of 1340°F and a pressure of 10 atmospheres, equilibrium predicts only CaS via reaction (2). There is reason to believe that addition of a catalyst will enhance the rate of reaction (2) at temperatures below 1500°F(2).

A separate discussion based on the results of a literature survey of reaction (3) is enclosed in Appendix X, Part M, for ready reference.

V. Process Descriptions

A. One Step Regeneration Process

The one step regeneration flow sheet contains four sections:

- Combustor
- Lime Regenerator
- Sulfur Plant
- H_2S Plant

In the combustor, the SO_2 formed from combustion of sulfur-bearing coal is absorbed in a fluidized lime bed via the following reaction:

$$CaO_{(s)} + SO_{2(g)} + 1/2\ O_{2(g)} \rightleftarrows CaSO_{4(s)}$$

Sulfated lime (i.e., $CaSO_4$) from the combustor is transferred to the regenerator where it is reduced to lime via the reaction:

$$CaSO_{4(s)} + \begin{bmatrix} CO \\ H_2 \end{bmatrix}_{(g)} \rightleftarrows CaO_{(s)} + SO_{2(g)} + \begin{bmatrix} CO_2 \\ H_2O \end{bmatrix}_{(g)}$$

Off gas from the regenerator containing SO_2 is cooled, mixed with a gas rich in H_2S, and sent to the sulfur plant where the Claus reaction produces elemental sulfur:

$$2H_2S_{(g)} + SO_{2(g)} \rightleftarrows 2H_2O_{(g)} + 3S_{(g)}$$

Some of the sulfur produced in the sulfur plant is then sent to the H_2S plant where the following two reactions are carried out:

$$CH_{4(g)} + 4S_{(g)} \rightleftarrows CS_{2(g)} + 2H_2S_{(g)}$$

$$CS_{2(g)} + 2\ H_2O_{(g)} \rightleftarrows CO_{2(g)} + 2\ H_2S_{(g)}$$

H_2S from this step is then mixed with the regenerator off gas and fed to the sulfur plant as described above.

Figures 1 and 2 are the process flow diagrams illustrating the one step regeneration process which utilizes either a high pressure or a low pressure regeneration scheme. The chemistry and the process flows for the two cases are virtually identical, and for this reason only one material balance and one flow sheet are provided. The primary difference in the two cases is in the handling of solids between the combustor and the regenerator; this will be discussed in a separate section. Stream summaries for this process are presented in Table 1.

Pulverized coal dispersed in air is transported to the bottom of the combustor vessel D-101, above a grid plate provided to insure even distribution of gas over the vessel cross section. (Note that coal grinding equipment is not shown.) Combustion air from compressor J-101 as well as a recycle gas stream from the sulfur plant tail gas compressor J-201 are introduced below the grid. A more detailed drawing of the combustor-regenerator circuit is presented later (Figures 5 & 6). Coal combustion occurs in a fluidized bed of lime with 15% excess air at 1700°F and 150 psia. Immersed in the bed and surrounding the bed are heat exchanger tubes which extract the heat of combustion by generation of high pressure steam. The sulfur in the coal is initially oxidized to SO_2 in the bottom of the bed and then absorbed by the lime to produce $CaSO_4$. A make-up stream of fresh limestone ($CaCO_3$) is introduced directly into the combustor bed as is a recycle stream of regenerated lime. The fresh limestone is required to maintain the activity of the lime bed. It undergoes calcining directly upon entering the combustor bed:

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

Combustion gases from the bed exit through a cyclone where entrained lime particles and large fly ash particles are separated before the gases reach the turbine and economizer. Small fly ash particles pass through with the flue gas.

Rock, containing CaO and $CaSO_4$ (str. 1)*, is transported from the combustor bed to the regenerator, D-102, where the $CaSO_4$ is reduced to CaO in a fluidized bed at 2000°F and 40 psia (152 psia in the high pressure case). Reducing gas at 2680°F (str. 6), formed by the partial oxidation of natural gas with air in combustion chamber B-101, is introduced below the regenerator grid. Immediately above the grid more air is added such that the total air added is 80% of that necessary for the complete combustion of the natural gas. It is necessary to withhold some of the air from B-101 in order to limit the temperature rise of the gas below the grid to a level which is acceptable from a materials of construction standpoint. Regenerated rock (str. 2) is returned to the combustor after a small slipstream of rock (str. 3) is removed.

Gas from the reduction reaction (str. 7) containing 7.5% SO_2 and 28.6% H_2O, passes through a cyclone to separate entrained lime, and then through a cooling train (C-100, 101, 101A, 102) where the gas is cooled from 2000°F to 100°F and water is condensed. The heat removed from stream 7 is used to reheat steam from the first stage of the power plant steam turbine in C-100 and generate 1000 psig steam in C-101 and C-101A. Water is condensed in C-102 and is separated from the gas in drum F-101. Water is condensed at this point in an attempt to improve the yield of elemental sulfur in the sulfur plant. It was felt that this processing scheme would improve the Claus Plant efficiency. However, no attempt was made to optimize the

* Refers to stream numbers in Table 1

system and it is possible that the Shell method (Shell Report, April, 1972, Figure 2, which was not available to M.W. Kellogg) which does not include condensing water before feeding the Claus reactors is more economical. After H_2O condensation, a gas from the H_2S section (str. 30) containing approximately 80% H_2S is blended with the regenerator off gas and the mixture is heated to 169°F in C-103 by exchange with hot gas (str. 28) from hydrolysis reactor D-302, and then to 425°F in C-105 by exchange with hot gas from incinerator B-201. At 425°F the gas is ready for entry into the Claus reactors for sulfur production.

In the sulfur plant, the blended gas from the reheat train passes through two reactors, D-201 & D-202 where sulfur is formed by the Claus reaction. Referring to Figure 2, gas from the reheater, C-105, passes through reactor D-201 where heat from the exothermic reaction raises the temperature to 743°F. The gas from the first reactor is cooled to 375°F by exchange in reheat exchanger C-201 with cool gas coming from F-201 and in C-203 via 50 psig steam generation. Sulfur is condensed in C-203. Gas from drum F-201 (str. 14) is reheated to 425°F in C-201 and reacted to produce more sulfur in D-202. Hot gas from D-202 is cooled to 300°F in C-203 where sulfur condenses and the resulting liquid-gas mixture then flows into F-202 where liquid sulfur is separated and recovered.

Gas from F-202, containing some sulfur vapor as well as unreacted H_2S and SO_2 is sent to a natural gas fired combustion chamber, B-201. In B-201, H_2S and sulfur vapor are oxidized at 1450°F to SO_2. This is necessary because the incinerated gas is eventually fed to combustor D-101 for SO_2 removal.

Hot gas from B-201 (str. 18) is cooled in C-105 by exchange with sulfur plant feed and in C-204, C-204A and C-205 by generation of 100 psig steam and exchange with cooling water. Water is condensed in C-205 to save compressor horsepower and separated in F-203. From here cooled gas goes to J-201 where it is compressed to 153 psia. The compressed gas (str. 20) is fed back into the combustor D-101 where residual SO_2 is absorbed and eventually returned to the sulfur plant.

The net sulfur product from F-201 and F-202 is pumped to a sulfur storage pit. The rest of the sulfur production (str. 21) however, is sent to the H_2S plant. Molten sulfur (str. 21) is pumped to heater F-301, where the temperature is raised from 300°F to 500°F in a non-flow, stirred tank heater. This type heater is necessary in order to avoid pumping sulfur through a shell and tube exchanger at a temperature range in which sulfur has peculiar viscosity characteristics. Liquid sulfur from F-301 is pumped through B-301 where sulfur is vaporized and heated to 1165°F. Furnace B-301 also preheats a CH_4 feed stream (str. 23) to 760°F. The preheated CH_4 and sulfur vapor are mixed and fed to CS_2 reactor D-301 where the following reaction occurs:

$$CH_{4(g)} + 4\ S_{(g)} \rightleftharpoons CS_{2(g)} + 2\ H_2S_{(g)}$$

Heat released by the reaction raises the temperature of the outlet gas (str. 24) to 1229°F. Outlet gas from D-301 is cooled to 248°F by exchange in sulfur heater F-301 and C-301

and C-302. Condensed sulfur is separated from reactor effluent gas in F-302. From here unreacted sulfur is recycled to the reactor (D-301) via F-301 where it is reheated. Separator overhead gas (str. 25) is reheated in C-301 to 600°F and mixed with steam (str. 27) prior to entering the hydrolyzer reactor, D-302. The following reaction occurs in the hydrolyzer:

$$CS_{2(g)} + 2\ H_2O_{(g)} \rightleftarrows CO_{2(g)} + 2\ H_2S_{(g)}$$

Since the above reaction is strongly exothermic, it is necessary to limit the temperature rise of the exit gas (str. 28) to 600°F by generating 150 psig steam in D-302. Product gas from D-302, containing approximately 11% H_2O, is cooled in C-103 by exchange with sulfur plant feed gas. Water is condensed in C-104 raising the H_2S concentration in the gas from F-102 to about 80%. From this point the gas (str. 30) is mixed with regenerator off gas and fed to the sulfur plant.

M.W. Kellogg chose technology currently available for conversion of sulfur to H_2S via first producing CS_2. No attempt was made to find the lowest cost method of producing the H_2S required for the Claus reaction. It is possible that H_2S may be produced directly from SO_2 eliminating the need to recycle sulfur but this was not investigated.

B. Two Step Regeneration Process

The second process to be described is the two step regeneration process. This process contains the following basic sections:

- Combustor
- First stage and second stage lime regenerators
- Amine treating unit
- Sulfur plant

The principle of operation of the combustor remains the same as in the previously discussed one step process and, for this reason, will not be discussed again. The basic difference between the two processes is in the regeneration of $CaSO_4$; two regeneration steps are used in this instance and sulfur is released as H_2S rather than SO_2. Only pressurized regenerator operation was considered because it was found that the chemistry of the second regeneration step required high pressure. In the first stage of regeneration sulfated lime from the combustor is reduced to CaS via the reaction:

$$CaSO_{4(s)} + 4 \begin{bmatrix} CO \\ H_2 \end{bmatrix}_{(g)} \rightleftarrows CaS_{(s)} + 4 \begin{bmatrix} CO_2 \\ H_2O \end{bmatrix}_{(g)}$$

CO_2 produced in the above step is recovered in an amine absorber and is subsequently used as a reactant in the second stage regenerator where CaS is reacted to $CaCO_3$ by the reaction:

$$CaS_{(s)} + CO_{2(g)} + H_2O_{(g)} \rightleftarrows Ca\,CO_{3(s)} + H_2S_{(g)}$$

H_2S produced in the second stage is cooled and sent directly to a conventional sulfur plant where 1/3 of it is oxidized to SO_2:

$$H_2S_{(g)} + 3/2\ O_{2(g)} \rightleftarrows SO_{2(g)} + H_2O_{(g)}$$

The SO_2 produced from the above then takes part in the Claus reaction to produce elemental sulfur:

$$2H_2S_{(g)} + SO_{2(g)} \rightleftarrows 2H_2O_{(g)} + 3S_{(g)}$$

Stream summaries for the 2-step process are presented in Table 2. Referring to Figure 3, sulfated rock from the combustor (str. 1) is transported to the first stage regenerator where it is contacted with hot reducing gas (str. 7) resulting from the partial oxidation of CH_4 with 60% of theoretical air in combustion chamber, B-101. Gas from B-101 must be

cooled in order to maintain the first stage regenerator (D-102) in heat balance at the relatively low temperature of 1340°F. This is accomplished by generating steam and preheating boiler feed water in C-101 and C-101A followed by exchanging with gas (str. 9) from the CO_2 compressor, J-102. Rock from D-102 (str. 2) containing CaS is transported from the first stage to the second stage regenerator and exiting gas (str. 8) containing CO_2 and H_2O goes to the amine absorber, D-301.

From the overhead of the first stage regenerator, str. 8 is cooled from 1340°F to 150°F by reboiling amine solution in C-301 and by exchanging with cooling water in C-303. Water is condensed in C-303 and is separated in F-301. Dry gas from F-301 (str. 11) goes to the amine absorber, D-301, where some of the CO_2 and essentially all of the trace of H_2S contained in the gas is removed by contact with a circulating amine solution. Rich amine solution at 148°F from the bottom of the absorber exchanges heat with lean solution from the bottom of the stripper, D-302, and goes to the top of the stripper where CO_2 and the small amount of H_2S present are flashed overhead. Lean solution from the bottom of the stripper is cooled from 245°F to 110°F by exchange with rich solution in C-304 and cooling water in C-306. Lean gas leaves the top of the absorber at about 115°F and goes to the stack. CO_2 and traces of H_2S from drum F-302 go to CO_2 compressor J-102 where the gas is boosted from 20 psia to 1 [illegible] psia. Steam is added to the compressed CO_2 to bring the H_2O composition up to 50% (str. 9). From J-102 the gas goes to C-102 where it is heated to 471°F for entry into the second stage regenerator, D-103. In the second stage regenerator, the rock which overflows from the first stage at 1340°F is contacted with the gas from C-102 containing equimolar amounts of CO_2 and H_2O along with some traces of H_2S which were produced in the first stage. Gas (str. 9) enters below a grid plate which is provided to give good distribution over the vessel cross section. Gas (str. 10) exits from the second stage at 980°F and contains about 16% H_2S and 42% H_2O.

cooled in order to maintain the first stage regenerator (D-102) in heat balance at the relatively low temperature of 1340°F. This is accomplished by generating steam and preheating boiler feed water in C-101 and C-101A followed by exchanging with gas (str. 9) from the CO_2 compressor, J-102. Rock from D-102 (str. 2) containing CaS is transported from the first stage to the second stage regenerator and exiting gas (str. 8) containing CO_2 and H_2O goes to the amine absorber, D-301.

From the overhead of the first stage regenerator, str. 8 is cooled from 1340°F to 150°F by reboiling amine solution in C-301 and by exchanging with cooling water in C-303. Water is condensed in C-303 and is separated in F-301. Dry gas from F-301 (str. 11) goes to the amine absorber, D-301, where some of the CO_2 and essentially all of the trace of H_2S contained in the gas is removed by contact with a circulating amine solution. Rich amine solution at 148°F from the bottom of the absorber exchanges heat with lean solution from the bottom of the stripper, D-302, and goes to the top of the stripper where CO_2 and the small amount of H_2S present are flashed overhead. Lean solution from the bottom of the stripper is cooled from 245°F to 110°F by exchange with rich solution in C-304 and cooling water in C-306. Lean gas leaves the top of the absorber at about 115°F and goes to the stack. CO_2 and traces of H_2S from drum F-302 go to CO_2 compressor J-102 where the gas is boosted from 20 psia to 154 psia. Steam is added to the compressed CO_2 to bring the H_2O composition up to 50% (str. 9). From J-102 the gas goes to C-102 where it is heated to 471°F for entry into the second stage regenerator, D-103. In the second stage regenerator, the rock which overflows from the first stage at 1340°F is contacted with the gas from C-102 containing equimolar amounts of CO_2 and H_2O along with some traces of H_2S which were produced in the first stage. Gas (str. 9) enters below a grid plate which is provided to give good distribution over the vessel cross section. Gas (str. 10) exits from the second stage at 980°F and contains about 16% H_2S and 42% H_2O.

From the second stage, rock containing CaO and $CaCO_3$ is returned to the combustor after a small slip stream of rock is purged. In the combustor, the $CaCO_3$ made in the second stage undergoes rapid calcining to produce CaO and CO_2.

From the second stage, overhead gas goes to a cooling train (Fig. 4) which condenses H_2O prior to entry to the sulfur plant. Gas is cooled from 980°F to 345°F by generating steam in C-103 and preheating boiler feed water in C-103A. Gas is cooled from 345°F to 100°F in C-104 by exchange with cooling water. Condensed water is separated in F-201 and the dry gas (str. 14) is reheated to 450°F in C-105 by exchange with gas from incinerator B-201 (str. 15).

Gas from C-105 at 450°F is fed to a conventional sulfur plant which is not shown in detail in Figure 4. This sulfur plant would be similar to the one in Figure 2 with the exception that a furnace would be included to oxidize 1/3 of the entering H_2S to SO_2. The reactor and condenser sequence would be the same as in Figure 2. Molten sulfur from the condenser flows to a storage pit. Gas from the sulfur plant final condenser, containing unreacted H_2S and SO_2, goes to the tail gas incinerator, B-201. In the incinerator which operates at 1400°F, sulfur present in the tail gas is oxidized to SO_2. Hot gas from the incinerator (str. 15) is cooled from 1400°F to 120°F before going to recycle compressor J-201 where the gas is boosted to 153 psia and sent to the combustor for removal of residual SO_2. Hot gas (str. 15) is cooled by exchanging with sulfur plant feed in C-105 and then generating 100 psig steam and preheating boiler feed water in C-201 and C-201A. Water is condensed from the gas by exchange with cooling water in C-202.

As mentioned in the description of the 1-step process, water is condensed from the Claus plant feed gas in an attempt to improve efficiency of the sulfur recovery system. However, again no effort was made to optimize the process

and it is possible that it is not necessary to condense water before feeding the Claus plant.

C. Special Equipment for Sulfur Condensation

A special sequence of processing steps is required to avoid exchanger plugging in the event elemental sulfur is present in the off gas from the 2nd stage regenerator in the case of the 2-step process, or the regenerator of the 1-step process (see Figures 1, 4). As the processes were originally described, any traces of sulfur present in the off gas from the regenerators would be condensed and solidified at 100°F thereby causing plugging in exchanger tubes. No process calculations have been made for this section of equipment; rather a method of handling the problem has been indicated. All temperatures and flow rates shown on the regenerator effluent cooling trains of Figs. 1 and 4 are based on the assumption that no elemental sulfur is present at this point. The following description applies to both regeneration processes.

Gas, at about 400°F containing elemental sulfur, enters the bottom of a baffled tower. Here gas is contacted with a cold slurry of solid sulfur and water, thereby cooling the gas and causing water to condense and sulfur to solidify. Slurry is pumped from the bottom of the baffle tower, through a cooler, and back to the top of the tower. A slip stream of slurry is withdrawn upstream of the cooler and is sent to a centrifuge where the slurry is concentrated. From the centrifuge, concentrated slurry goes to a stirred heating tank maintained at a temperature high enough to cause the sulfur to liquefy and the remaining water to flash overhead. Water flashed overhead, containing some sulfur vapor, is sent to the bottom of the baffle tower. Molten sulfur from the heating tank is pumped to a pit.

VI. Discussion of Solids Handling

In order to provide a realistic appraisal of how a regenerable limestone process might work in practice, preliminary diagrams of the combustor/regenerators and their associated solids handling circuits have been prepared. It is felt that although many details have not been considered (materials of construction, gas distributor design, etc.) and considerable experimental work is still to be performed, the fundamentals of the schemes presented are sound.

Three regeneration schemes are illustrated: (A) one step regeneration with pressurized combustor and low pressure regenerator, (B) one step regeneration with pressurized combustor and high pressure regenerator, and (C) two step regeneration with pressurized combustor and pressurized regenerators.

A. One Step Regeneration - low pressure case

Figure 5 is a diagram of how the combustor and regenerator are envisioned to operate in this case. Pulverized coal is conveyed to one of two feed hoppers, H-1 or H-1A. At all times one feed hopper is depressurized and is receiving coal from the conveyor, and one hopper is feeding coal to the combustor at a controlled rate while under air pressure via a line to the discharge of the air compressor, J-101. Such a system of alternating pressurized feed hoppers is referred to as a lock hopper system. Coal is fed to the combustor at a controlled rate through rotary feeders located in the bottom of H-1 and H-1A. Pressurized air from J-101 picks up the coal from the rotary feeders and transports it in dilute phase to the upper side of the combustor grid. Combustion air from J-101 and sulfur plant tail gas from J-201 are introduced below the grid and pass up through the grid into the fluidized lime bed (150 psia) where combustion occurs. In all three cases the combustor vessel was assumed to have a cylindrical geometry for convenience sake although the eventual shape of a commercial size unit may be different.

Heat exchanger tubes immersed in the fluidized lime bed extract combustion heat through generation of high pressure steam. Preheated boiler water is fed into the steam drum which is a "doughnut" shaped bustle pipe surrounding the combustor. Water from the steam drum circulates through the tubes by thermosyphon action and is heated to its boiling point. Steam from the drum is superheated in a tube section which is located above the dense bed in the dilute phase. Gases from coal combustion pass up from the dense bed a distance equal to the transport disengaging height for entrained solids. At this point, gases with a residual amount of entrained solids enter an enlarged section of the combustor which houses a cyclone. In the cyclone, large rock and coal particles are separated from the gas. Air is introduced on the upstream side of a slide valve in the standpipe, thereby keeping the downmoving solids fluidized at a density of about 40 pounds per cubic foot (#/cf) and returned to the bed, while small fly ash particles exit the cyclone with the flue gas. Combustion gases pass from the cyclone to a turbine (not shown) for power extraction.

Sulfated lime from the fluidized combustor bed is withdrawn via an aerated standpipe which extends through the grid and out of the vessel. From the standpipe, solids drop into the sulfated lime hoppers, H-3 and H-3A. These are lock hoppers which, in essence, reduce the pressure between the combustor and the regenerator. Lock hoppers are required for this service rather than a slide valve alone because the high pressure drop would result in severe valve erosion. The method of operation of these hoppers is similar to that of the coal feed hoppers. When receiving sulfated lime, the hoppers are vented to the combustor to reduce the pressure drop across the slide valve. When feeding lime to the regenerator, the hoppers are vented to the regenerator to reduce the pressure drop across the rotary feeder. Lime being fed to the regenerator goes through the rotary feeder to be picked up by steam and transported in dilute phase to the regenerator fluidized bed. The density in the transport

line is 1#/cf.

Reducing gas is introduced into the regenerator (D-102) below a grid which is provided to distribute the gas over the vessel cross section. In the regenerator bed, $CaSO_4$ is reduced to CaO at 2000°F. A small amount of rock is withdrawn from the regenerator, via an aerated standpipe which extends through the grid to a slurry tank. This prevents a buildup of rock which would result from the constant addition of fresh limestone. In the slurry tank a small stream of water is mixed with the withdrawn rock to make a pumpable mixture containing 10 wt% solids. Alternatively, the solids could be withdrawn using a dry system. Gases from the reduction process pass up the regenerator vessel a distance of 30 ft. (equal to the transport disengaging height). Gas, containing residual solids, then passes from the regenerator to an external cyclone where solids are removed and returned to the dense bed. An external cyclone is possible in the low pressure regenerator case due to the relatively low pressure differential across the cyclone walls.

Regenerated rock is withdrawn from the regenerator via an aerated standpipe which drops lime into the regenerated lime hoppers H-2 and H-2A. These are lock hoppers which serve to build up pressure between the regenerator and combustor and operate in the manner previously described. In addition to receiving regenerated lime, the hoppers also receive a small flow of fresh limestone which helps to maintain a constant sorbent activity level. It is likely that some of the fresh limestone will calcine when mixed with 2000°F lime from the regenerator. Gas from the calcining reaction would pass through a vent to the atmosphere. From H-2 and H-2A, regenerated lime is fed to the combustor via rotary feeders at the bottom of the hoppers. From here air transports the lime in dilute phase to the combustor bed.

B. One Step Regeneration - high pressure case

Figure 6 illustrates the principle of operation of this case. The essential difference between this case and the previous low pressure case, as far as solids handling is concerned, is the elimination of one set of lock hoppers. Since the combustor is in no way different in this case from the low pressure case, it will not be discussed again.

Sulfated lime is removed from the combustor, D-101, via an aerated standpipe which extends through the combustor grid and the combustor plenum chamber directly below the grid. Solids from the standpipe, at a density of 40#/cf, pass through a slide valve which has a pressure drop of 2 psi. Downstream of the valve, solids are transported by steam at a density of 10#/cf to the regenerator D-102 which operates at 153 psia. Reducing gas from the partial oxidation of CH_4 is introduced below the grid and passes through the fluidized bed where $CaSO_4$ is reduced to CaO at 2000°F. From the bed, gas passes up a distance of 29 ft. (equal to the transport disengaging height) to an internally mounted cyclone which separates residual solids. An internal cyclone is used in this case to avoid the high pressure difference which would result from the cyclone being mounted externally. A small slipstream of rock is removed from the regenerator via an aerated standpipe to a slurry tank which is vented to the regenerator. Water is added to the slurry tank to make a 10% slurry. Slurry flows from the tank, through a valve, to an evaporation pond. Alternatively, the solids could be withdrawn using a dry system.

Regenerated solids are withdrawn from D-102 via an aerated standpipe. Solids pass through a slide valve, which takes a 2 psi pressure drop, and are picked up by air which transports solids back to the combustor at a density of 10#/cf. A measured amount of fresh limestone is added to the combustor via lock hoppers H-2 and H-2A. Fresh limestone passes through

rotary feeders and is introduced to the combustor bed via dilute phase transport with air.

C. Two Step Regeneration

The two step regeneration scheme is diagrammed in Figure 7. Only pressurized regenerators were considered in the two step regeneration process and therefore, only one solids handling diagram is presented. Here, as before, the principle of operation of the combustor remains the same as was described in (A), and therefore will not be discussed. Sulfated lime is withdrawn from the combustor via an aerated standpipe and transported to the first stage regenerator (D-102), in the manner that was discussed for the one step regeneration-pressurized regenerator case (B). Reducing gas from the partial oxidation of CH_4 enters the bottom of the first stage below a distribution grid and passes through a fluidized bed operating at 1340°F and 153 psia where $CaSO_4$ is reduced to CaS. Gas then passes through an internally housed cyclone where entrained solids are separated and returned to the bed via the cyclone dipleg.

Rock from the bed of the first stage is withdrawn via an aerated "lateral" to the upper bed of the second stage regenerator, D-103, which operates at 980°F and 150 psia. Regeneration gas (containing CO_2 and H_2O) enters the bottom of D-103 below a grid, and passes up through the bottom of the first of two beds, then through another distribution grid, and finally through the top bed. After passing through the top bed, gas enters an expanded section of D-103 where entrained solids settle out. No cyclone is provided for the 2nd stage regenerator since a relatively small diameter (3 ft) expanded section will allow settling of all but the finest particles. Solids from the upper bed descend to the lower bed via an aerated downcomer. Solids from the bottom bed of the second stage are returned to the combustor via a standpipe which extends through the bottom grid. Solids pass through a slide

valve and are transported to the combustor in dilute phase by air. A small slipstream of rock is withdrawn from the bottom bed of D-103, slurried, and sent to an evaporation pond in a procedure similar to that previously discussed. Alternatively, the solids could be withdrawn using a dry system as mentioned in the 1-step process description.

Fresh limestone is added to the combustor via lock hoppers H-2 and H-2A in the same way as described in Section (B).

VII. Process Design Notes

A. Combustor Design Bases

In order to perform a process design, certain basic assumptions had to be made regarding the size of the boiler (and thus the size of the lime regeneration and sulfur recovery plants) and the SO_2 absorption capacity of the lime bed. In doing this, data and information were taken from Esso Research and Engineering Interim Report, January 1, 1971-June 1, 1971) contract CPA 70-19 (3). Definition regarding the scope of the entire study was taken from M.W. Kellogg letter No. K-9-3 dated February 8, 1972.

Conforming with the above documents, a boiler size of 15 MW was taken as a basis for calculations in both the 1-step and 2-step regeneration schemes. Using a heat rate of 10,000 Btu/hr-KW as a first approximatation, a feed rate of 11,539 #/hr of 4.5% sulfur coal was determined assuming a coal heating value of 13,000 Btu/lb. Using the coal feed rate initially determined, a heat balance on the boiler was made assuming 15% excess air for combustion and a flue gas outlet temperature of 200°F. In this way a required heat rate of 9,607 Btu/hr-KW was calculated. Table 3 shows the results of the heat balance for the 1-step regeneration process. Although the 2-step process would have a slightly different heat balance as a result of the regenerated rock being cooler than in the 1-step process, and the recycle gas being a smaller volume, the effect would be negligible in the total balances, and not worthy of consideration. In addition, it is advantageous for evaluation purposes to keep the coal feed rate, and thus the SO_2 release rate, the same for the two process schemes.

In both regeneration schemes, 90% removal efficiency of all sulfur entering the combustor was assumed for design purposes as this was the standard removal referred to in the Esso report. This means that when there is a recycle stream containing SO_2, such as the sulfur plant tail gas, the net removal efficiency based on sulfur in the entering coal is lower than 90%. Thus as a result of the recycle of sulfur plant tail gas, only 88.6% of the sulfur in the entering coal is recovered.

In order to determine the required circulation of rock between the combustor and regenerator, it is necessary to know the CaO utilization at 90% SO_2 removal defined as:

$$(CaO)_{90} = \frac{\text{mols } CaSO_4}{\text{mols } (CaO + CaSO_4)} \times 100$$

The $(CaO)_{90}$ has an inverse relationship to particle size; as particle size increases more solid is required on a weight basis to perform a given desulfurization. It was originally intended to use 20% utilization of CaO; however, this required a relatively small size lime particle (1000μ) which in turn would have required a very low superficial velocity to avoid enormous entrainment rates. As an alternative, the lime particle size was increased to 2000μ and assumed to have a size distribution similar to that of lime N-1359 on page 15 of the Esso report (3). The chemical composition of the lime was taken from page 12 of the above report. Associated with this, a utilization of 7.6% was used, based on the Esso report (3), page 46, Table 6. A limestone makeup of 10% of the stoichiometric requirement was used. A superficial gas velocity of 6 ft/sec was chosen for the combustor to avoid unreasonable entrainment rates.

Calculation of the flue gas composition and volume was made using the Pittsburgh bituminous coal composition given in the Esso report (3) Pg. 14, Table 2 - ultimate analysis, adjusted to 4.5% sulfur.

B. Regenerator Calculations

For both the 1-step and 2-step regeneration schemes, the composition of the rock withdrawn from the bed and the gas leaving the bed for all regeneration reactions was determined by assuming that the reactions proceeded to chemical equilibrium. This was made necessary by complete lack of kinetic data. In doing this an internal computer program which predicts the equilibrium composition of reacting systems was modified and debugged for use with the solid-gas reaction systems. This program, which was developed by Kellogg, solves for equilibrium compositions by minimizing the total free energy of the reacting system. This circumvents the necessity of identifying individual reactions in a complex system and has the advantage of being completely rigorous.

In making equilibrium calcualtions for the 1-step process a temperature of 2000°F was found to be desirable from the standpoint of suppressing the CaS formation. Atmospheric pressure and 150 psia were examined for effect and, at the ratio of reactants used, no significant difference in equilibrium composition could be seen between the two pressures. Table 4 presents the pertinent reaction conditions for the 1-step process and the composition of the reducing gas and the product gas. Interestingly, past laboratory investigations at Esso Research and Engineering (1) have shown that the re-

duction of $CaSO_4$ with CO and H_2 is limited by equilibrium at 2000°F in a batch operated fluidized bed.

For the 2-step process it was found that the pressure effect was very important in the reaction:

$$CaS_{(s)} + CO_{2(g)} + H_2O_{(g)} \rightleftarrows CaCO_{3(s)} + H_2S_{(g)}$$

Increasing pressure increases the conversion. For this reason the 1st stage and 2nd stage regenerator pressures were chosen to approximate 150 psia, consistent with the combustor pressure. Tables 5 and 6 present the pertinent reaction conditions and the feed gas and product gas compositions for the 1st and 2nd stage regenerators.

C. Fluidized Vessel Calculations

Basically, the fluidized combustors and regenerators are sized to conform with the superficial velocities mentioned in the Esso report (3). Table 7 summarizes the dimensions and the design parameters which were calculated for all of the fluidized vessels. Only one combustor is listed since this vessel is the same size for both regeneration schemes.

The calculation procedures used to generate the data are discussed below:

1. Minimum Fluidization Velocity - Care was taken to see that the minimum fluidization velocity was less than one-half the normal superficial velocity on all vessels, thereby allowing for a 50% turndown ratio. The value of the minimum fluidization velocity was determined by the method of Leva (4):

$$G_{MF} = 688\, D_P^{1.82} \frac{[\rho_f\ (\rho_s - \rho_f)]^{0.94}}{\mu^{0.88}}$$

$$U_{MF} = G_{MF}/\rho_f$$

where,

G_{MF} = fluid mass velocity for minimum fluidization, lb/hr-ft^2

U_{MF} = minimum fluidization velocity, ft/sec.

D_p = particle diameter, ft.

ρ_f, ρ_s = fluid, solids density, lb/ft^3

μ = fluid viscosity, lb/ft-sec.

2. Slugging Height - The slugging height is defined as the bed height at which gas bubbles passing up the bed grow to the size of the containing vessel diameter. Since such large bubbles can set up vibrational forces, bed heights were kept below the slugging height. The correlation of Yagi and Muchi (5), developed for particle sizes greater than 100 microns, was used to calculate the slugging height:

$$L_{sh} = 1.18\ D_t\ (D_p \rho_s)^{-0.3}$$

where

L_{sh} = slugging height, ft.

D_t = vessel diameter, ft.

3. Transport Disengaging Height - (TDH) This is defined as the height above the bed at which entrainment has decreased to a constant value. It is important to know this parameter for proper placement of cyclones; it has been shown (5) that the economic optimum height above a dense bed for the location of cyclone inlets is the TDH. The correlation of Zenz and Weil (6), relating TDH to vessel diameter and gas superficial velocity, was used in this study.

4. Solids Entrainment - Considering 2000μ lime particles alone, there should be no entrainment above the TDH since the lime particle terminal velocities for pressurized and atmospheric operations are 19 ft/sec. and 72 ft/sec. compared to superficial velocities of 6 and 7 ft/sec. Considering, however, that smaller sized coal and fly ash will be present in the combustor bed and possibly the regenerator beds (not to mention attrited lime), it is evident that entrainment can occur above the TDH. Esso Research and Engineering (3) was able to calculate some entrainment rates (pg. 78) by assuming a bed composition of 80% lime, 17% fly ash and 3% coal. With this as a basis, they calculated an entrainment rate of 5 lb/min at 50 ft. outage for their 15 in. combustor at a superficial velocity of 7 ft/sec. The combustor entrainment rate reported in Table 7 was calculated using the above Esso number but corrected for a higher pressure. This rate of entrainment results in a combustor cyclone loading of 669 gr/ft^3 which is acceptable. It was not possible to calculate entrainment rates for the regenerator vessels although it is likely that there would be some as a result of some coal and fly ash being present in the sulfated lime transported from the combustor to the regenerator(s).

As can be seen from Table 7 the combustor and 2nd stage regenerator (2-step process) are provided with expanded upper sections. In the case of the combustor, this was done in order to make room for the cyclone. In the case of the 2nd stage regenerator, it was done to reduce the velocity such that no cyclone would be necessary. Two beds are shown for the 2nd stage regenerator on Figure 3 as a result of the low maximum allowable bed height imposed by slugging limitations. This was entirely arbitrary and would or would not be necessary depending on the kinetics of the 2nd stage regeneration reaction.

D. H_2S Plant

The production of H_2S from molten sulfur and CH_4 as shown on Figure 2 represents no new technology. The following two reactions form the basis of the process as used in the 1-step regeneration scheme:

$$CH_{4(g)} + 4S_{(g)} \rightleftarrows CS_{2(g)} + 2\ H_2S_{(g)} \qquad (1)$$

$$CS_{2(g)} + 2H_2O_{(g)} \rightleftarrows CO_{2(g)} + 2\ H_2S_{(g)} \qquad (2)$$

CS_2 is produced commercially in large quantities via reaction (1) and the conditions used for it in this study were taken from the literature (7). The pertinent reaction conditions are as follows:

Temperature	1200°F
Space Velocity	560 (SCFH gas/CF catalyst)
Catalyst	Silica Gel
CH_4 Conversion	90%
Excess Sulfur	10%

The reaction is slightly exothermic, so that the effluent temperature is 1229°F.

The hydrolysis step, reaction (2), is also well established and is used to increase the yield of H_2S by hydrolyzing CS_2. The following reactor conditions were taken from the literature (8):

Temperature	600°F (outlet)
Contact Time	0.4 sec.
Catalyst	Activated Alumina
CS_2 conversion	100%
Excess Steam	32.6%

Reaction (2) is strongly exothermic (29,500 Btu/lb mol CS_2) and for this reason heat must be removed via steam generation to prevent an excessive temperature rise.

E. Sulfur Plant

The sulfur plant of the 1-step regeneration process shown in Figure 2 is a normal sulfur plant with some slight modifications. A typical sulfur plant feed gas contains sulfur as H_2S only, and for this reason, the plant must contain a furnace to oxidize 1/3 of the entering H_2S to SO_2 as required by the Claus reaction stoichiometry:

$$2\ H_2S_{(g)} + SO_{2(g)} \rightleftarrows 2\ H_2O_{(g)} + 3S_{(g)}$$

Since the sulfur plant feed in the 1-step regeneration process already contains SO_2 and H_2S in the proper proportions, the furnace is not necessary.

The sulfur plant for the 1-step process therefore consists of only the two Claus reactors, two condensors, and one reheat exchanger. Technical information and procedures for calculating the conversions and temperatures around the sulfur reactors of Figure 2 were taken from the Pan American Petroleum Corporation sulfur plant design manual. Since details of this process are of a proprietary nature, the calculation procedures cannot be discussed.

The acid gas feed to the sulfur plant of the 2-step regeneration process contains only H_2S and for this reason a conventional sulfur plant is applicable. Details are not shown on Figure 4 since this is a well known process not requiring special discussion.

A sulfur removal efficiency of 90% was assumed for purposes of material balance calculations.

In both the 1-step and 2-step processes it was assumed to be desirable to have the entering acid gas as dry as possible in order to increase the Claus reaction equilibrium conversion. For this reason, the regenerator off gas was cooled to 100°F in both cases.

VIII. Process Appraisals

A. Comparison of the processes

Since no cost estimating has been done, and no attempt at process optimization has been made, meaningful comparisons between the 1-step and 2-step regeneration processes are difficult to make. Despite this, some general comments can be made in surveying the two processes.

1. Utilities - Listed below are the utilities which were calculated for the two regeneration processes. There was essentially no difference in utilities between the low pressure and high pressure cases of the 1-step regeneration process.

	1-step	2-step
Steam generation, lb/hr	5,394	13,050
Steam consumption, lb/hr	605	2,647
CTW consumption, gpm (exclusive of compressors)	241	861
Electrical power consumption, KW (for compressors only)	7,556	7,461
Natural gas consumption, SCFH (exclusive of sulfur plants)	10,700	34,400

The higher steam generation rate for the 2-step process results from having to cool the large volume of 1st stage reducing gas in order to maintain the proper heat balance in the 1st stage regenerator, D-102. In addition, the conventional sulfur plant generates more steam than the modified sulfur plant because it has a furnace for oxidation of H_2S in the feed gas with an attendant waste heat boiler. The net steam export, represented by steam generation minus steam consumption, is about twice as high for the 2-step process versus the 1-step process. The higher natural gas consumption for the 2-step process results from the large amount of reducing gas required in the 1st stage regenerator. Power consumption for compressors is nearly equal, even though the 2-step process requires three compressors and the 1-step process requires two.

2. Solids Handling and Operability - In comparing the low pressure and high pressure cases of the 1-step regeneration process it can be seen that the low pressure case requires one more set of lock hoppers and solids feeders than the high pressure case. In addition to this, a larger regenerator and a larger cyclone are required for the low pressure case.

In comparing the 1-step and 2-step regeneration processes, it should be noted that the lime particles will be cycled over wider temperature extremes between the combustor and regenerators in the 2-step process (1700°F to 980°F) than in the 1-step process (1700°F to 2000°F). This could have detrimental effects on the maintenance of lime reactivity in the combustor. In addition to this, the $CaCO_3$ coming from the 2nd stage regenerator in the 2-step process will be subjected to flash calcining in the combustor. This also could have implications with regard to lime reactivity in the combustor.

3. Processing Steps - The advantage of the 2-step process lies in its ability to remove sulfur as H_2S, obviating the need for the H_2S generating facility. Balancing this, however, the 2-step process has a more involved regeneration scheme, additional equipment in the sulfur plant (furnace), an amine system for recovery of CO_2, and higher consumption of natural gas for regeneration.

B. Areas Requiring Further Investigation

During the course of the study it became evident that certain potential problems regarding the combustor and regenerator would need to be resolved before a final process design could be performed. In most instances this information would need to be obtained through laboratory investigation on a continuously operating combustor/regenerator. Listed below is a discussion of the various areas which are considered to be problematical.

1. Fly Ash - An important topic for investigation concerns the fate of the fly ash formed from combustion of coal. Presumably some of the fly ash initially elutriated from the bed contains unburned carbon which must be returned to the bed for burning in order to obtain full heating value from the coal. With this in mind two possibilities exist; (1) fly ash will elutriate from the bed, be captured by the cyclone, and be returned to the bed over and over until the heating values have been removed from the fly ash and it is such a size that it exits from the cyclone with the flue gas and, (2) fly ash recycles from the bed to the cyclone and back to the bed at such a rate that the cyclone becomes overloaded and relatively large fly ash particles containing unburned carbon exit with the flue gas. If the second situation developed, a high temperature carbon burnup cell might be needed to cut down the amount of recycle by insuring that fly ash would be captured only once by the cyclone, and subsequently would be burned in the cell

to a size which would permit it to escape the cyclone on the next pass.

Another area for concern regards the fly ash dust load on the turbine blades. Since for maximum power extraction, the high pressure gas entering the turbine should be hot (1700°F), it will not be possible to remove all entrained fly ash by conventional means (electrostatic precipitators and bag filters require temperatures no higher than approximately 800°F and 300°F respectively). It should be possible to remove some of the fly ash upstream of the turbine with high efficiency externally mounted cyclones downstream of the internally mounted, "rough cut" cyclone. Technology however, would need to be developed for turbine blades which could handle gas at 1700°F which still contained some dust.

Another problem related to fly ash in the 1-step process regards its possible action in the lime regenerator. Since the combustor bed will contain a certain steady-state amount of fly ash, especially in the upper part of the bed, it is likely that some fly ash will be withdrawn with the sulfated lime and be sent to the regenerator. Here, at 2000°F, there might be a possibility of slag formation. It is not known what the effect of this would be, but it is likely that proper fluid bed operation would be interfered with. In the event of slag formation, provisions for removing it would be required; otherwise regenerator temperatures below the ash fusion point would be needed.

Another area for concern regarding fly ash in both the 1-step and 2-step processes is that the carbon and hydrogen remaining on it would be reformed in the regenerator to form CO and H_2; this is an endothermic reaction which could have a large effect on regenerator heat balance depending

on the amount of carbon present and the extent to which reforming occurred. To counter this heat effect, more air would be introduced with the same amount of natural gas indicated on the flow sheet thereby increasing the reducing gas inlet temperature to the regenerator (1st stage regenerator in the case of the 2-step process).

2. Lime Attrition - In the process description a method for purging lime from the system was described in which reactivated lime was withdrawn from the regenerator (2nd stage regenerator in the case of the 2-step regeneration process), slurried with water in a tank, and sent to an evaporation pond. In actual practice, attrition of lime particles and subsequent loss of fines through the cyclones may make the purge unnecessary and indeed, the fresh limestone makeup rate might need to be increased over that indicated to maintain a constant solids inventory in the system. Data on lime attrition, therefore, need to be obtained.

3. Kinetics of Regeneration - The most obvious lack of data is in the area of lime regeneration kinetics. It has been mentioned that regenerator effluent streams shown on Figures 1 and 3 were computed by assuming that the reactions occurred at equilibrium. At the high temperature (2000°F) of the 1-step regeneration process this may be a good assumption; however, at the lower temperatures of the 2-step process (1340°F and 980°F) such an assumption could be far from correct. Therefore, kinetic data on the three reactions which were used in this study need to be obtained.

The regenerator on Figure 1 and the 1st stage regenerator on Figure 3 are indicated to be single beds. In actuality it may be necessary to provide staged beds (as shown on Figure 3 for the 2nd stage regenerator) in order to obtain higher conversions. The 2nd stage regenerator is shown as having two beds, not for kinetic reasons, but because of the relatively low bed heights which can be used before the

onset of slugging.

Of interest regarding the 2-step process is a patent (2) describing a method of catalyzing the 1st stage regenerator reaction:

$$CaSO_{4(s)} + 4 \begin{bmatrix} CO \\ H_2 \end{bmatrix}_{(g)} \rightleftharpoons CaS_{(s)} + 4 \begin{bmatrix} CO_2 \\ H_2O \end{bmatrix}_{(g)}$$

According to the patent, the above reaction is accelerated when a small amount (as low as 0.1 vol. %) of gas containing sulfur as S_2, SO_2, or a sulfide such as H_2S is added to the system. According to the patent, practice of the invention at a temperature as low as 1300°F is possible. In the 2-step regeneration process the patent could be applied by recycling a small amount of gas containing approximately 28% H_2S from F-201 on Figure 4 through a booster compressor and into the bed of the 1st stage regenerator D-102 on Figure 3. The H_2S accelerator would remain in the system since after leaving the regenerator it would be absorbed by amine solution in D-301. Here again, experimental work would be required to check the applicability of the patent.

4. Elemental Sulfur in Regenerator Effluent - Calculations made with the free energy minimization computer program showed that, theoretically, traces of elemental sulfur could be present in the effluent gas from the 2nd stage regenerator of the 2-step process and also the regenerator of the 1-step process. The reason for concern regarding elemental sulfur is that when the off gas from the regenerators is cooled to 100°F for water condensation, any sulfur present in the gas would condense and solidify thereby causing plugging problems in the condensers. Laboratory investigations will be required to determine if elemental sulfur will actually be present.

5. Trace Elements - The capture from coal of trace elements (such as chlorine) by lime in the combustor could lead to deactivation of the lime and consequently higher fresh limestone makeup rates or higher regenerated lime recycle rates. In order to evaluate this possibility, extended runs should be made on a continuously operated laboratory combustor/regenerator to check for contaminant buildup.

Using the free energy minimization computer program it was possible to theoretically investigate the fate of chlorine in the regenerators assuming that under the conditions existing in the combustor, the lime would capture the chlorine as $CaCl_2$. It was found for the 1-step process (at both high and low pressure) that $CaCl_2$ would not exist in the regenerator and that chlorine would exit with the regenerator off gas as HCl. For the 2-step process at 1340°F however, it was found that both $CaCl_2$ and HCl could exist.

5. Trace Elements - The capture from coal of trace elements (such as chlorine) by lime in the combustor could lead to deactivation of the lime and consequently higher fresh limestone makeup rates or higher regenerated lime recycle rates. In order to evaluate this possibility, extended runs should be made on a continuously operated laboratory combustor/regenerator to check for contaminant buildup.

Using the free energy minimization computer program it was possible to theoretically investigate the fate of chlorine in the regenerators assuming that under the conditions existing in the combustor, the lime would capture the chlorine as $CaCl_2$. It was found for the 1-step process (at both high and low pressure) that $CaCl_2$ would not exist in the regenerator and that chlorine would exit with the regenerator off gas as HCl. For the 2-step process at 1340°F however, it was found that both $CaCl_2$ and HCl could exist.

IX. References

1. Bertrand, R.R. et al, Fluid Bed Studies of The Limestone Based Flue Gas Desulfurization Process, Interim Report, October 15, 1967 - February 15, 1969, submitted to National Air Pollution Control Administration under Contract No. PH 86-67-130.

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7. Folkins, H. O., et al., Carbon Disulfide from Natural Gas and Sulfur, Ind. Eng. Chem., 42, 2202-2207 (1950).

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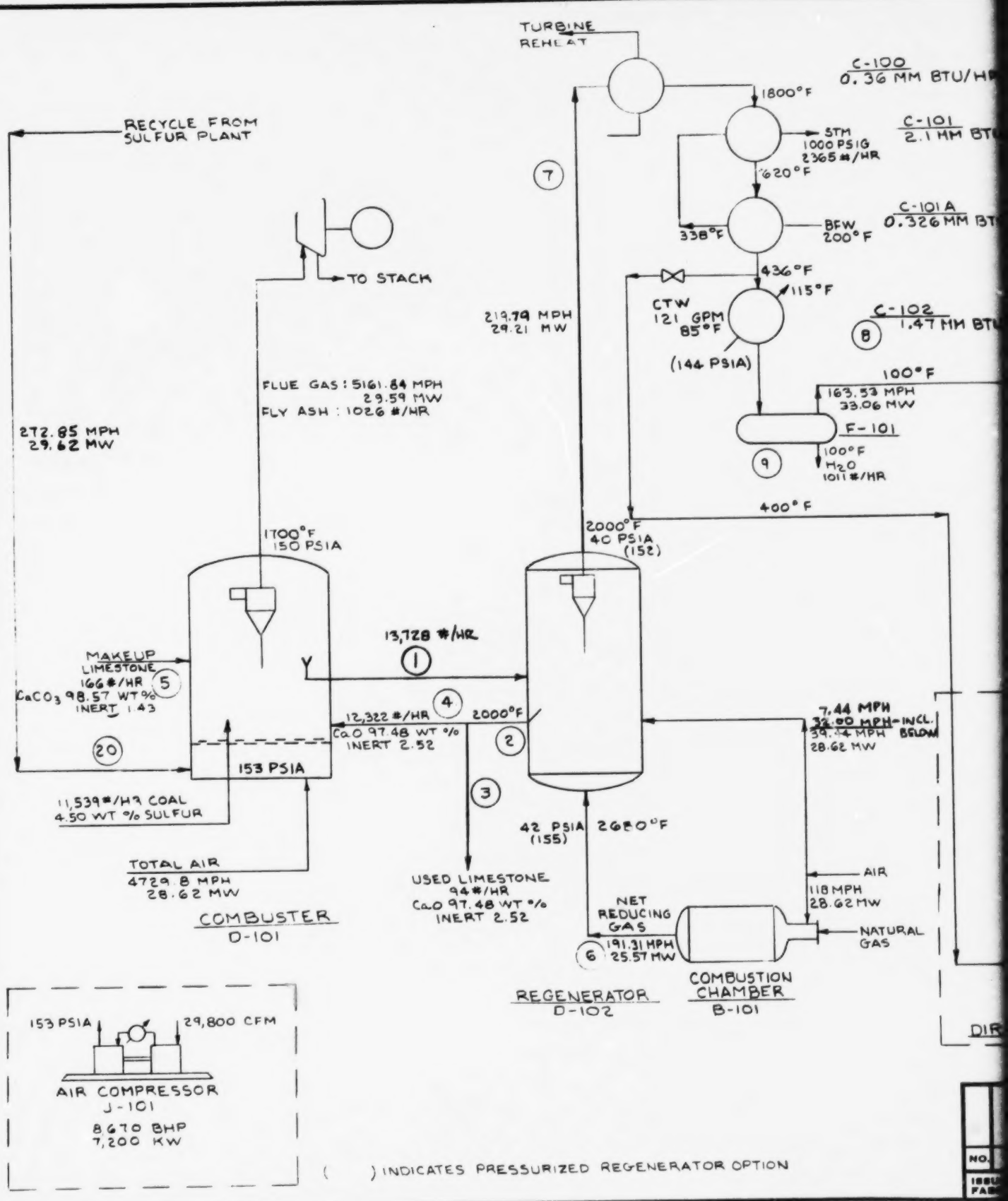
X. Appendices

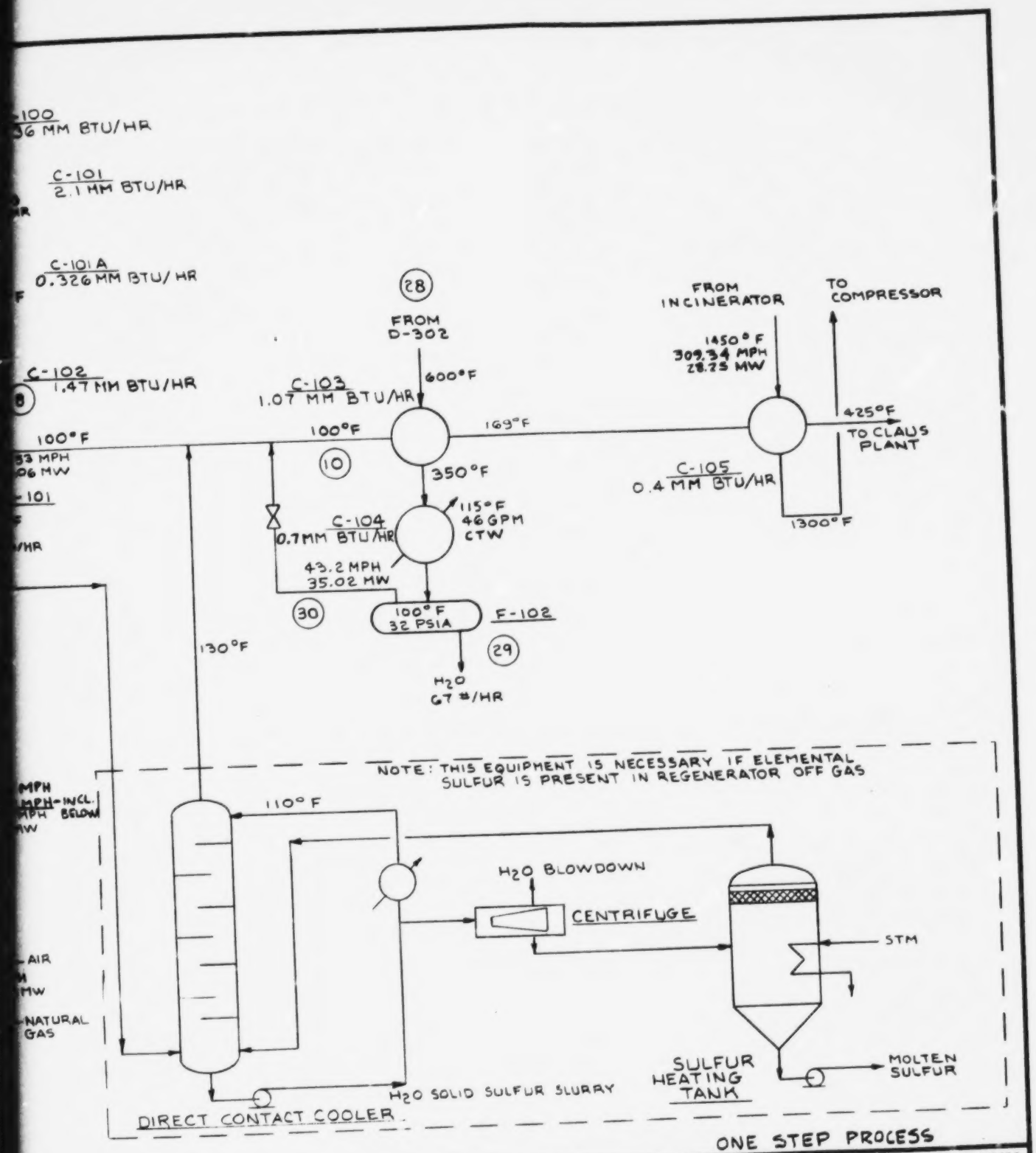
Appendix A



B
11 X 17

DEFIANCE NO. 1000H

A



NO.	REVISION DESCRIPTION	DATE	BY	CHK.

ISSUED FOR FABRICATION

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SCALE: –
DRAWN: BCB
CHECKED:
APPROVED:
DATED:

THE M. W. KELLOGG COMPANY
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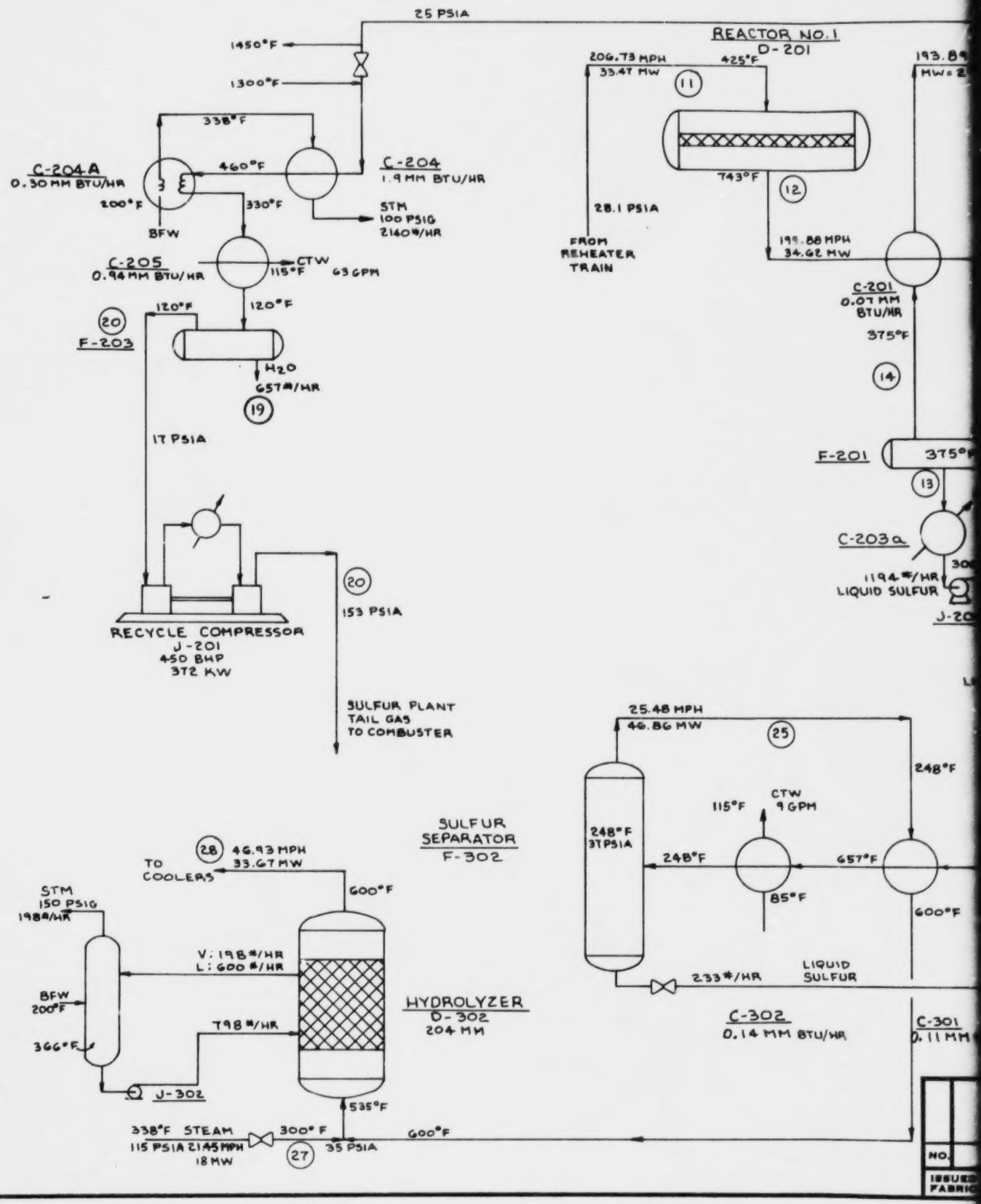
REGENERABLE LIMESTONE PROCESS

FIG. 1

CLASS	AREA	JOB NO.	DRAWING NO.

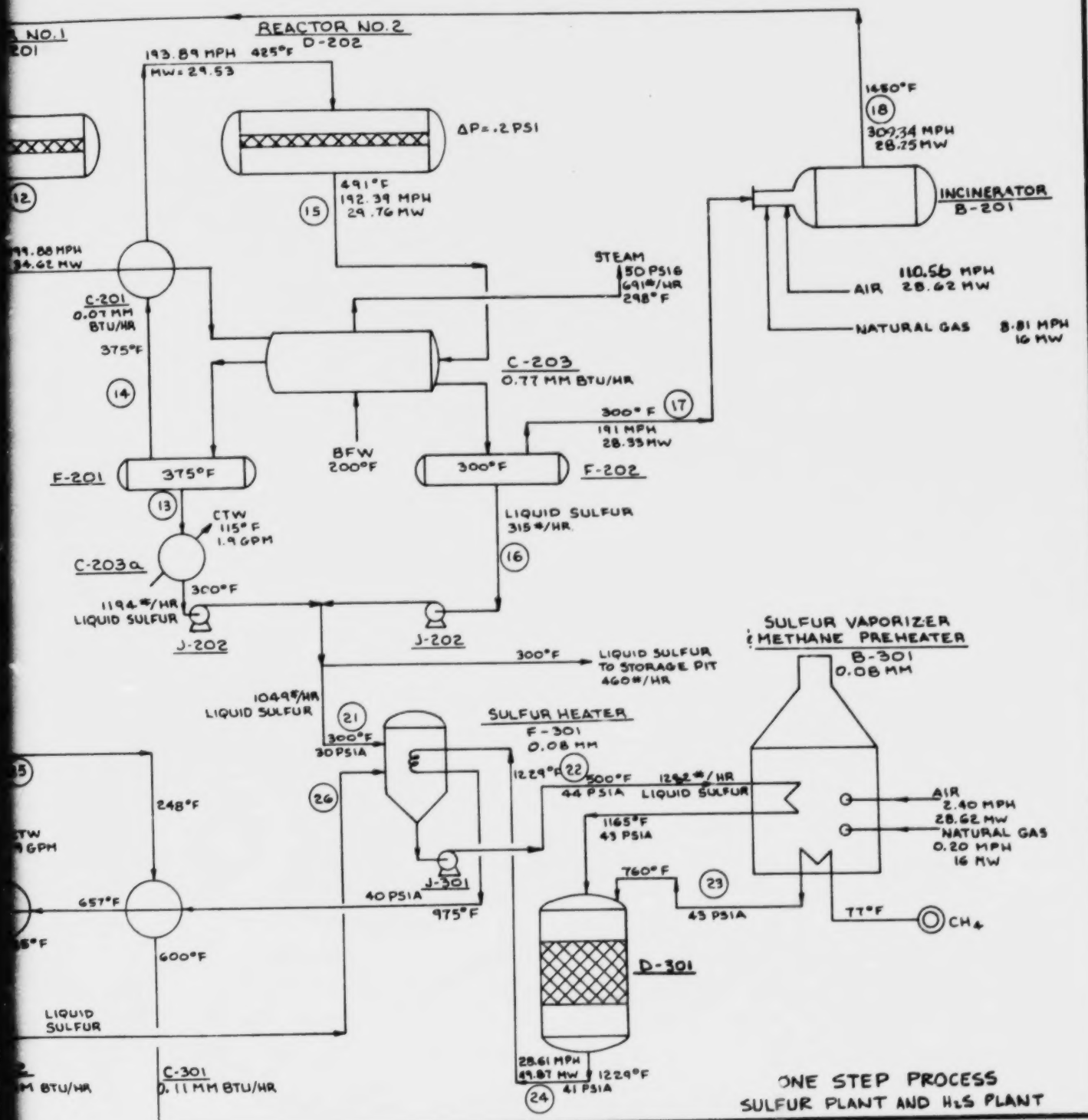
B

Appendix B


25 PSIA
1450°F
1300°F
338°F
C-204A
0.30 MM BTU/HR
460°F
C-204
1.9 MM BTU/HR
200°F
330°F
BFW
STM
100 PSIG
2140#/HR
C-205
0.94 MM BTU/HR
CTW
115°F
63 GPM
120°F
120°F
20
F-203
H2O
657#/HR
19
17 PSIA
RECYCLE COMPRESSOR
J-201
450 BHP
372 KW
20
153 PSIA
SULFUR PLANT
TAIL GAS
TO COMBUSTER
REACTOR NO.1
D-201
206.73 MPH
33.47 MW
425°F
11
743°F
12
28.1 PSIA
FROM
REHEATER
TRAIN
199.88 MPH
34.62 MW
C-201
0.07 MM
BTU/HR
375°F
14
F-201
375°F
13
C-203a
1194#/HR
LIQUID SULFUR
J-20
25.48 MPH
46.86 MW
25
248°F
CTW
9 GPM
115°F
248°F
37 PSIA
248°F
657°F
85°F
600°F
233#/HR
LIQUID
SULFUR
C-302
0.14 MM BTU/HR
C-301
0.11 MM
SULFUR
SEPARATOR
F-302
28
46.93 MPH
33.67 MW
TO
COOLERS
600°F
STM
150 PSIG
198#/HR
V: 198#/HR
L: 600#/HR
BFW
200°F
366°F
798#/HR
J-302
HYDROLYZER
D-302
204 MM
535°F
338°F STEAM
115 PSIA 2145 MPH
18 MW
300°F
27
35 PSIA
600°F
NO.
ISSUED
FABRIC

B
1 X 17

A



ONE STEP PROCESS
SULFUR PLANT AND H_2S PLANT

NO.	REVISION DESCRIPTION	DATE	BY	CHK.
	ISSUED FOR FABRICATION			
	ISSUED FOR CONSTRUCTION			

SCALE:
DRAWN: BCB
CHECKED:
APPROVED:
DATED:

THE M. W. KELLOGG COMPANY
a division of PULLMAN INCORPORATED

REGENERABLE LIMESTONE PROCESS

CLASS	AREA	JOB NO.	DRAWING NO.
			FIG. 2

B

ENG ADM 3 12-63

FOR

SUBJECT 1-step regen.

LOCATION

PAGE

EST. NO.

DATE

BY

TABLE 1
Stream Summaries

component	Str. 1 mph	Str. 1 lb/hr	Str. 2 mph	Str. 2 lb/hr	Str. 3 mph	Str. 3 lb/hr	Str. 4 mph	Str. 4 lb/hr
$CaSO_4$	16.40	2,233	-	-	-	-	-	-
CaO	199.39	11,182	215.84	12,104	1.64	92	215.80	12,012
CaS	-	-	-	-	-	-	-	-
$CaCO_3$	-	-	-	-	-	-	-	-
Inert		313		312		2		310
Total mph								
Total lb/hr		13,728		12,416		94		12,322
MW								
Temp °F	1700		2000		2000		2000	
Press. psia	40 (153)		40 (153)		40 (153)		150 (150)	
Transport Stm.	9.40 (8.33)	169 (150)	1.39 (1.39)	(25) (25)	1.39 (1.39)	(25) (25)		
Transport Air							103 (102)	2987 (2958)

( ) indicates pressurized regenerator option

TABLE 1 (Cont.)
Stream Summaries

	Str.	5
Component	mph	lb/hr
$CaSO_4$	-	-
CaO	-	-
CaS	-	-
$CaCO_3$	1.64	164
Inert		2
Total mph		
Total lb/hr		166
MW		
Temp. °F	77	
Press. psia	14.7 (150)	
Transport Stm.		
Transport Air	(4.5)	(131)

TABLE 1 (Cont.)
Stream Summaries

component	Str. 6 * mph	Str. 7 mph	Str. 8 mph	Str. 9 mph	Str. 10 mph	Str. 11 mph	Str. 12 mph	Str. 13 mph
CH_4	-	-	-	-	0.91	0.91	0.91	-
O_2	-	-	-	-	-	-	-	-
H_2	8.61	0.41	0.41	-	0.41	0.41	0.41	-
H_2O	42.45	62.77	6.51	56.26	7.95	7.95	34.17	-
CO_2	11.48	19.76	19.76	-	27.95	27.95	27.95	-
N_2	120.16	120.17	120.17	-	120.07	120.07	120.07	-
SO_2	-	16.35	16.35	-	16.35	16.35	3.24	-
H_2S	-	.02	.02	-	32.78	32.78	6.56	-
CO	8.61	.31	.31	-	0.31	0.31	0.31	-
CS_2	-	-	-	-	-	-	-	-
S_2	-	Trace	-	-	-	-	0.53	-
S_6	-	-	-	-	-	-	3.78	-
S_8	-	-	-	-	-	-	1.95	-
Liq. sulfur	-	-	-	-	-	-	-	37.31
Total mph	191.31	219.79	163.53	56.26	206.73	206.73	199.88	37.31
MW	25.57	29.21	33.06	18	33.47	33.47	34.62	32
Total lb/hr	4,892	6,418	5,407	1,011	6,920	6,920	6,920	1,194
Temp. °F	2,680	2,000	100	100	100	425	743	375
Press. psia	42 (155)	40 (152)	32 (144)	32 (144)	32	28	28	26

*composition and flow rate given is for net reducing gas above regenerator grid

TABLE 1 (Cont.)
Stream Summaries

Component	Str. 14 mph	Str. 15 mph	Str. 16 mph	Str. 17 mph	Str. 18 mph	Str. 19 mph	Str. 20 mph
CH_4	0.91	0.91	-	0.91	-	-	-
O_2	-	-	-	-	1.39	-	1.39
H_2	0.41	0.41	-	0.41	-	-	-
H_2O	34.17	39.42	-	39.42	60.58	36.49	24.09
CO_2	27.95	27.95	-	27.95	37.98	-	37.98
N_2	120.07	120.07	-	120.07	207.41	-	207.41
SO_2	3.24	0.61	-	0.61	1.98	-	1.98
H_2S	6.56	1.31	-	1.31	-	-	-
CO	0.31	0.31	-	0.31	-	-	-
CS_2	-	-	-	-	-	-	-
S_2	-	0.06	-	-	-	-	-
S_6	.069	0.47	-	.002	-	-	-
S_8	0.20	0.87	-	.006	-	-	-
Liq. sulfur	-	-	9.84	-	-	-	-
Total mph	193.89	192.39	9.84	191.0	309.34	36.49	272.85
MW	29.53	29.76	32	28.33	28.25	18	29.62
Total lb/hr	5,726	5,726	315	5,411	8,740	657	8,083
Temp. °F	375	491	300	300	1450	120	120
Press. psia	26	26	25	25	25	17	17/153

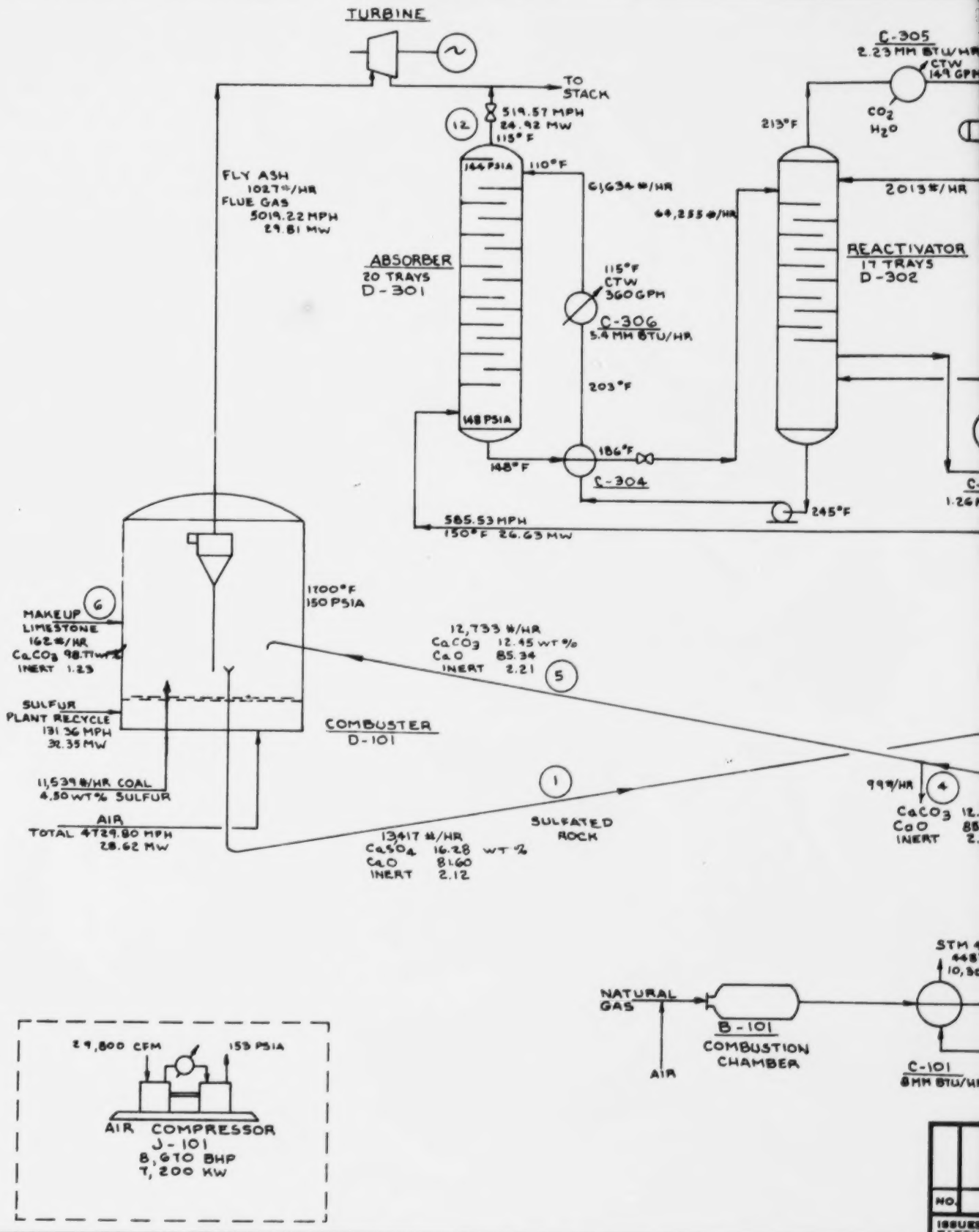
TABLE 1 (Cont.)
Stream Summaries

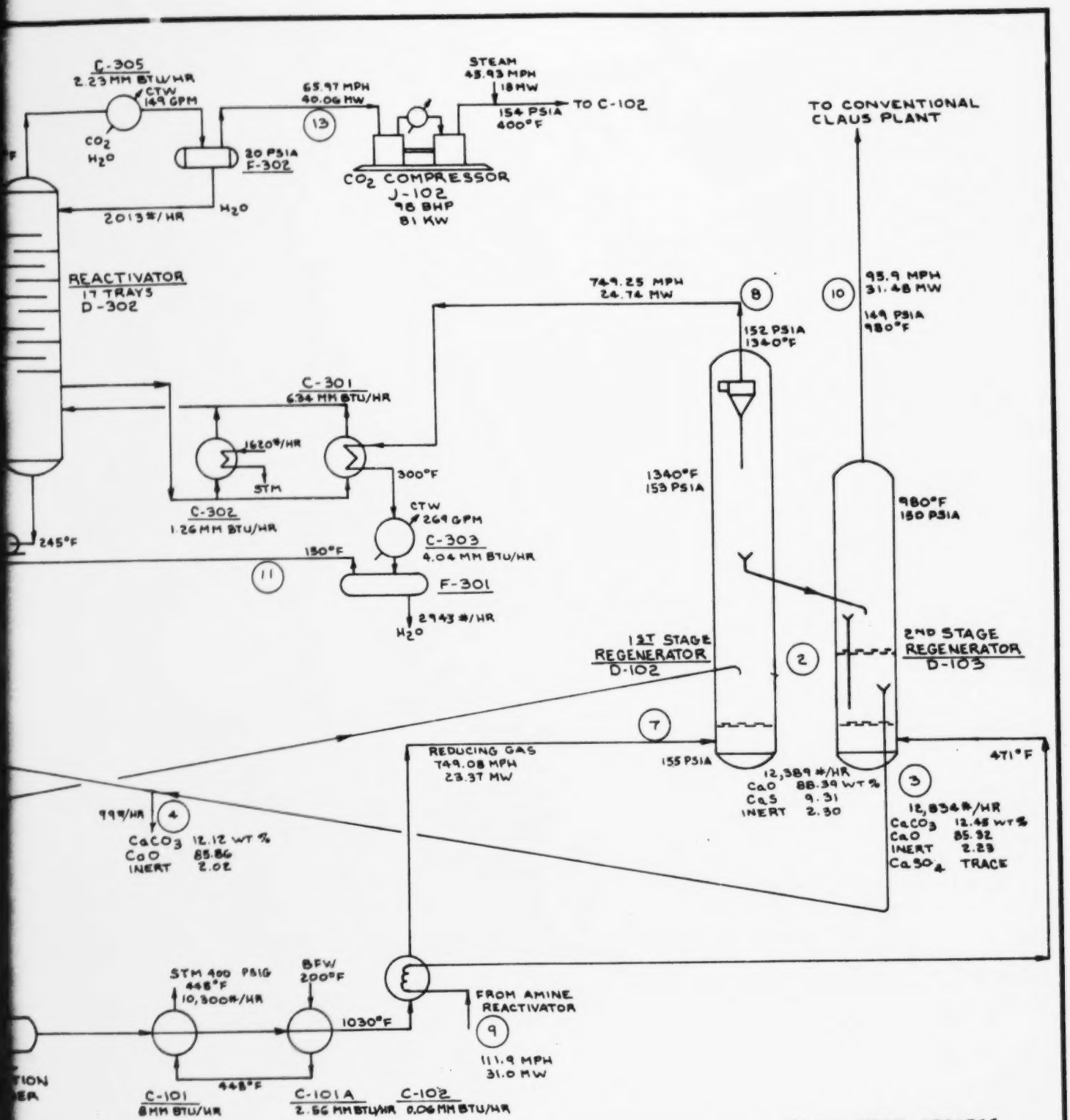
	Str. 21	Str. 22	Str. 23	Str. 24	Str. 25	Str. 26	Str. 27	Str. 28
component	mph	mph	mph	mph	mph	mph	mph	mph
CH_4	-	-	9.10	0.91	0.91	-	-	0.91
O_2	-	-	-	-	-	-	-	-
H_2	-	-	-	-	-	-	-	-
H_2O	-	-	-	-	-	-	21.45	5.07
CO_2	-	-	-	-	-	-	-	8.19
N_2	-	-	-	-	-	-	-	-
SO_2	-	-	-	-		-	-	-
H_2S	-	-	-	16.38	16.38	-	-	32.76
CO	-	-	-	-	-	-	-	-
CS_2	-	-	-	8.19	8.19	-	-	-
S_2	-	-	-	2.88	-	-	-	-
S_6	-	-	-	0.24	-	-	-	-
S_8	-	-	-	0.01	-	-	-	-
Liq. sulfur	32.77	40.05	-	-	-	7.28	-	-
Total mph	32.77	40.05	9.10	28.61	25.48	7.28	21.45	46.93
MW	32	32	16	49.87	46.86	32	18	33.67
Total lb/hr	1,049	1,282	146	1,427	1,194	233	386	1,580
Temp °F	300	500	760	1,229	248	248	300	600
Press. psia	30	44	43	41	37	30	35	33

TABLE 1 (Cont.)
Stream Summaries

Component	Str. 29 mph	Str. 30 mph
CH_4	-	0.91
O_2	-	-
H_2	-	-
H_2O	3.73	1.34
CO_2	-	8.19
N_2	-	-
SO_2	-	-
H_2S	-	32.76
CO	-	-
CS_2	-	-
S_2	-	-
S_6	-	-
S_8	-	-
Liq. sulfur	-	-
Total mph	3.73	43.20
MW	18	35.02
Total lb/hr	67	1,513
Temp. °F	100	100
Press. psia	32	32

Appendix D


TURBINE
TO STACK
519.57 MPH
24.92 MW
115°F
12
C-305
2.23 MM BTU/HR
CTW
149 GPM
CO_2
H_2O
213°F
FLY ASH
1027 #/HR
FLUE GAS
5019.22 MPH
29.81 MW
144 PSIA
110°F
61,634 #/HR
64,255 #/HR
2013 #/HR
ABSORBER
20 TRAYS
D-301
115°F
CTW
360 GPM
C-306
5.4 MM BTU/HR
REACTIVATOR
17 TRAYS
D-302
203°F
148 PSIA
186°F
148°F
C-304
245°F
585.53 MPH
150°F 26.63 MW
1700°F
150 PSIA
MAKEUP
LIMESTONE
162 #/HR
$CaCO_3$ 98.77 WT%
INERT 1.23
6
12,733 #/HR
$CaCO_3$ 12.45 WT%
CaO 85.34
INERT 2.21
5
SULFUR
PLANT RECYCLE
131.36 MPH
32.35 MW
COMBUSTER
D-101
11,539 #/HR COAL
4.50 WT% SULFUR
AIR
TOTAL 4729.80 MPH
28.62 MW
1
SULFATED
ROCK
13417 #/HR
$CaSO_4$ 16.28 WT %
CaO 81.60
INERT 2.12
999 #/HR
4
$CaCO_3$ 12.
CaO 85
INERT 2.
NATURAL
GAS
AIR
B-101
COMBUSTION
CHAMBER
C-101
8MM BTU/HR
29,800 CFM
153 PSIA
AIR COMPRESSOR
J-101
8,670 BHP
7,200 KW



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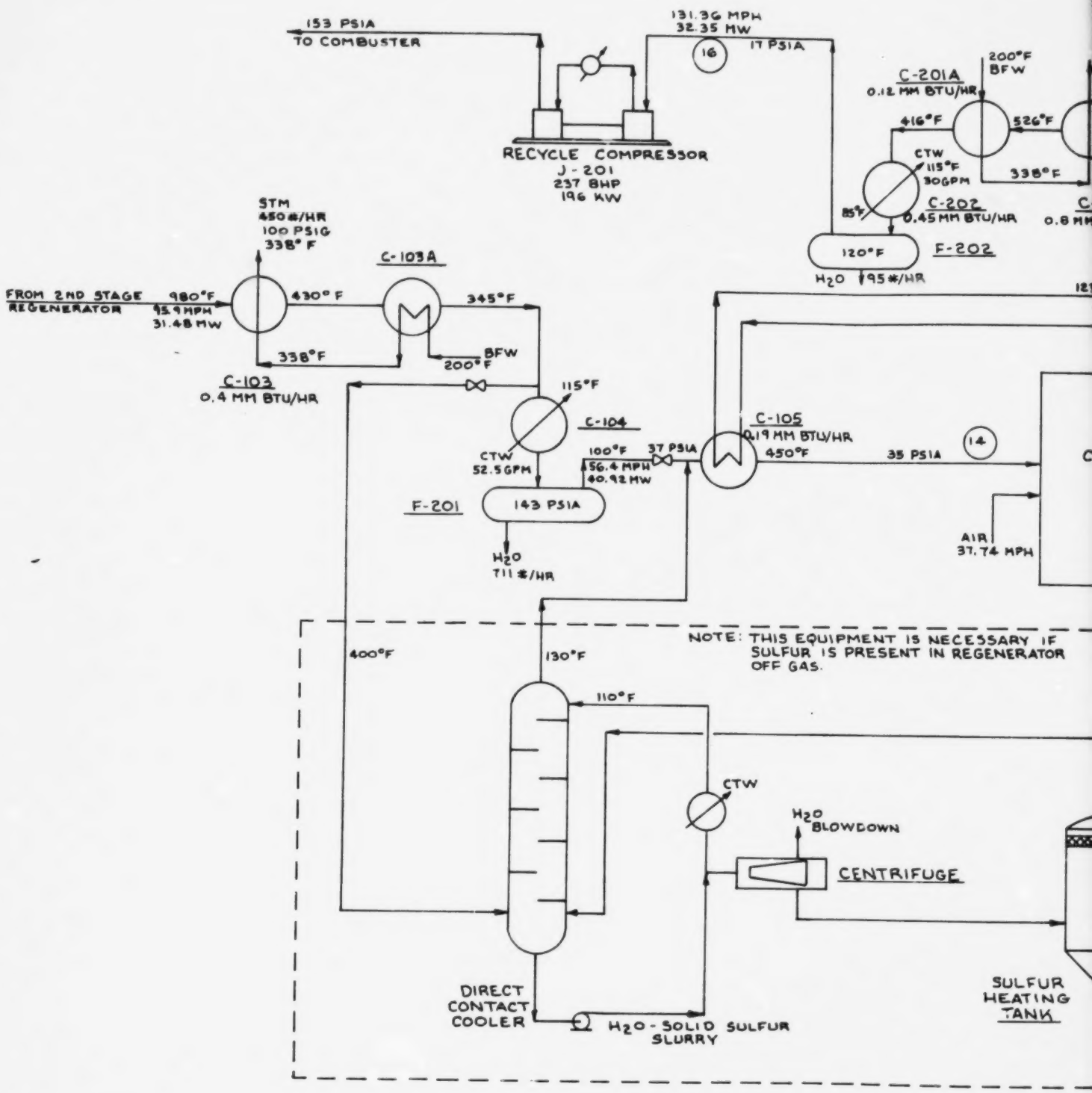
ALTERNATE PROCESS FOR THE RELEASE OF H_2S

CLASS	AREA	JOB NO.	DRAWING NO.
			FIG. 3

B

Appendix E



NO.	REVISION
	ISSUED FOR FABRICATION

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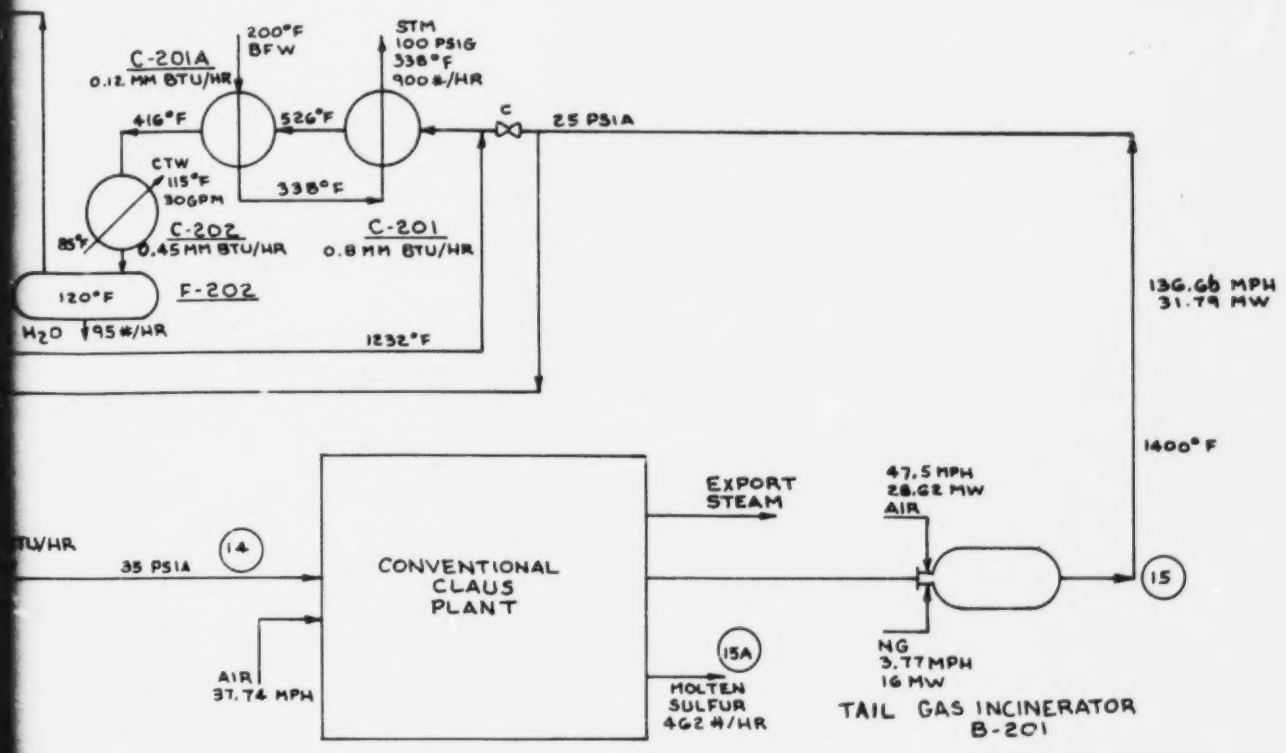

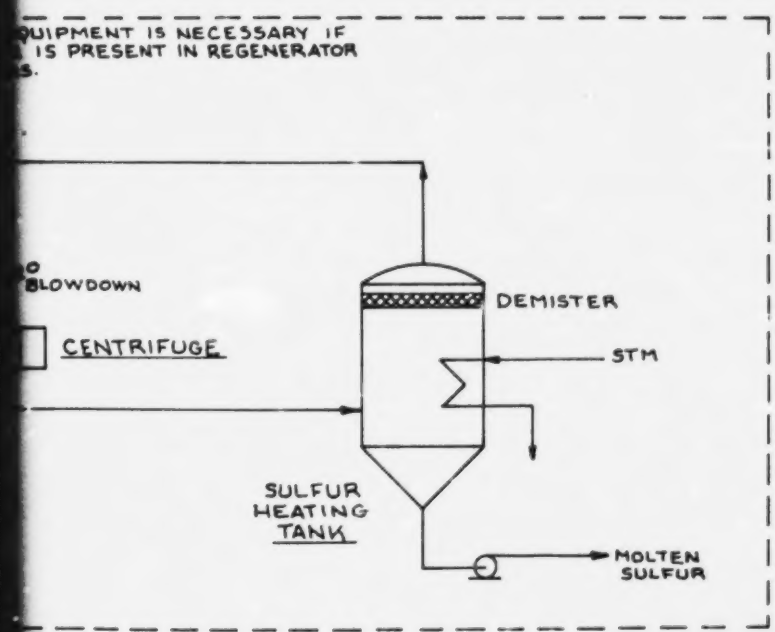

TWO STEP PROCESS
SULFUR PLANT

NO.	REVISION DESCRIPTION	DATE	BY	CHK.
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ALTERNATE PROCESS FOR
THE RELEASE OF H_2S

FIG. 4

CLASS	AREA	JOB NO.	DRAWING NO.

Appendix F

ENG ADM 3 12-63

FOR

SUBJECT 2-step regen.

LOCATION

PAGE

EST. NO.

DATE

BY

TABLE 2
Stream Summaries

	Str.	(1)	Str.	(2)	Str.	(3)	Str.	(4)
Component	mph	lb/hr	mph	lb/hr	mph	lb/hr	mph	lb/hr
$CaSO_4$	16.05	2,185	-	-	-	-	-	-
CaO	195.22	10,948	195.29	10,952	195.29	10,952	1.52	85
CaS	-	-	15.98	1,153	-	-	-	-
$CaCO_3$	-	-	-	-	15.97	1,598	.12	12
Inert		284		284		284		2
Total mph								
Total lb/hr		13,417		12,389		12,834		99
MW								
Temp. °F	1700		1340		980		980	
Press. psia	153		150		150		150	
Transport Steam	8.15	147	1.00	18	1.00	18	1.00	18
Transport Air	-	-	-	-	-	-		

TABLE 2 (Cont.)

Stream Summaries

	Str. (5)		Str. (6)	
Component	mph	lb/hr	mph	lb/hr
$CaSO_4$	-	-	-	-
CaO	193.78	10,867	-	-
CaS	-	-	-	-
$CaCO_3$	15.84	1,585	1.60	160
Inert		281		2
Total mph				
Total lb/hr		12,733		162
MW				
Temp. °F	980		77	
Press. psia	150		150	
Transport Steam				
Transport Air	12.10	351	4.35	126

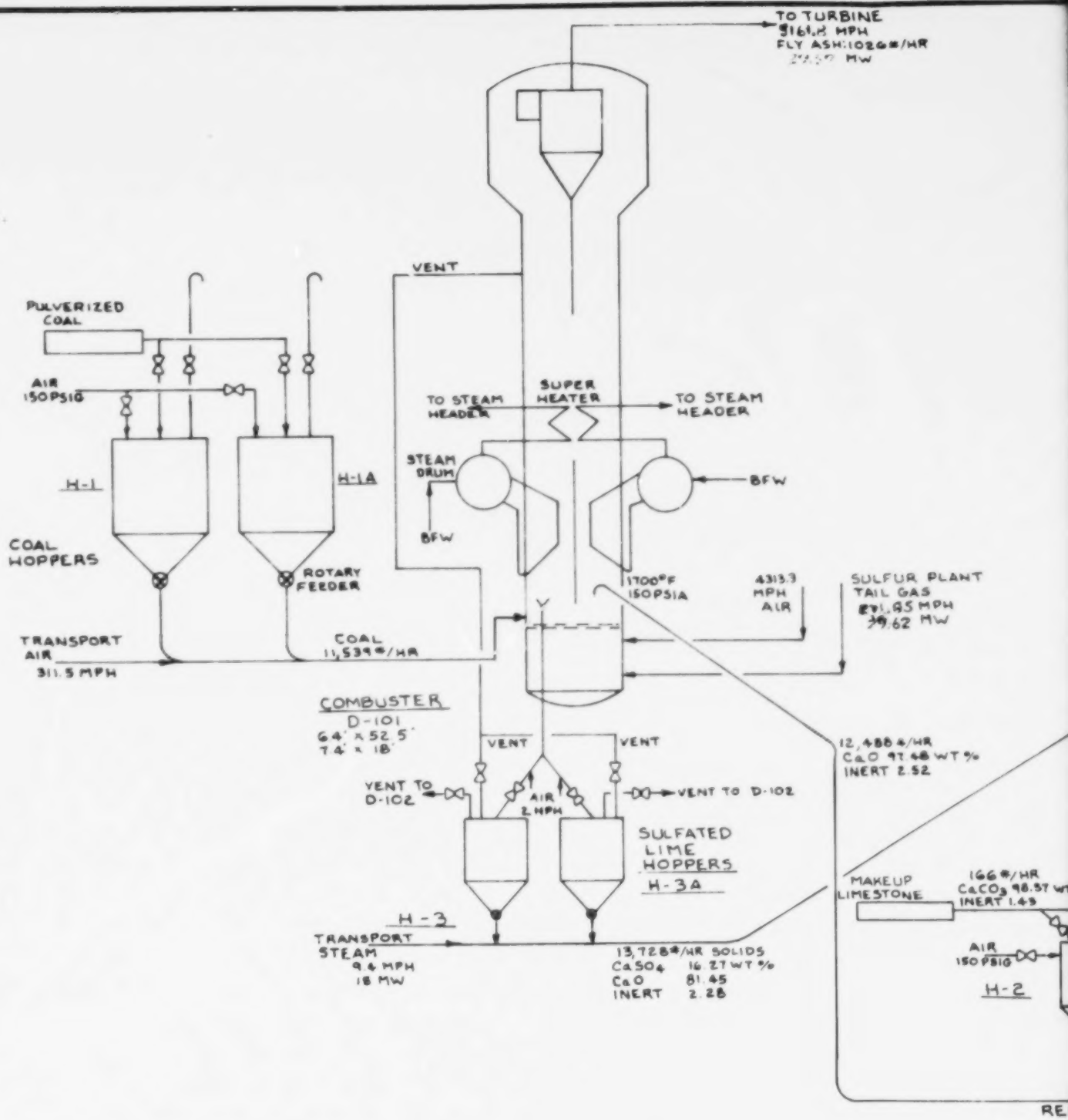
TABLE 2 (Cont.)
Stream Summaries

	Str. (7)	Str. (8)	Str. (9)	Str. (10)	Str. (11)	Str. (12)	Str. (13)	Str. (14)
Component	mph	mph	mph	mph	mph	mph	mph	mph
H_2S	-	0.08	0.08	15.86	0.08	-	0.08	15.86
CO_2	24.08	71.22	55.91	39.90	71.22	15.31	55.91	39.90
CO	67.42	20.27	-	0.03	20.27	20.27	-	0.03
H_2O	161.16	178.14	55.91	39.93	14.43	4.45	9.98	0.43
H_2	86.16	69.28	-	0.11	69.28	69.28	-	0.11
SO_2	-	-	-	0.02	-	-	-	0.02
S_2	-	-	-	0.05	-	-	-	0.05
Liq. Sulfur	-	-	-	-	-	-	-	-
N_2	410.27	410.25	-	-	410.25	410.25	-	-
O_2	-	-	-	-	-	-	-	-
Total mph	749.08	749.25	111.90	95.90	585.53	519.57	65.97	56.40
Total lb/hr	17,506	18,536	3,469	3,019	15,593	12,947	2,643	2,308
MW	23.37	24.74	31.00	31.48	26.63	24.92	40.06	40.92
Temp. °F	2680	1340	400	980	150	115	130	450
Press. psia	155	152	154	149	148	144	20	35

TABLE 2 (Cont.)
Stream Summaries

	Str. (15)	Str. (15a)	Str. (16)
Component	mph	mph	mph
H_2S	-	-	-
CO_2	43.72	-	43.72
CO	-	-	-
H_2O	24.07	-	18.77
H_2	-	-	-
SO_2	1.60	-	1.60
S_2	-	-	-
Liq. Sulfur	-	14.44	-
N_2	66.70	-	66.70
O_2	0.58	-	0.58
Total mph	136.66	14.44	131.36
Total lb/hr	4,344	462	4,249
MW	31.79	32	32.35
Temp. °F	1400	-	120
Press. psia	25	-	17/153

Appendix G



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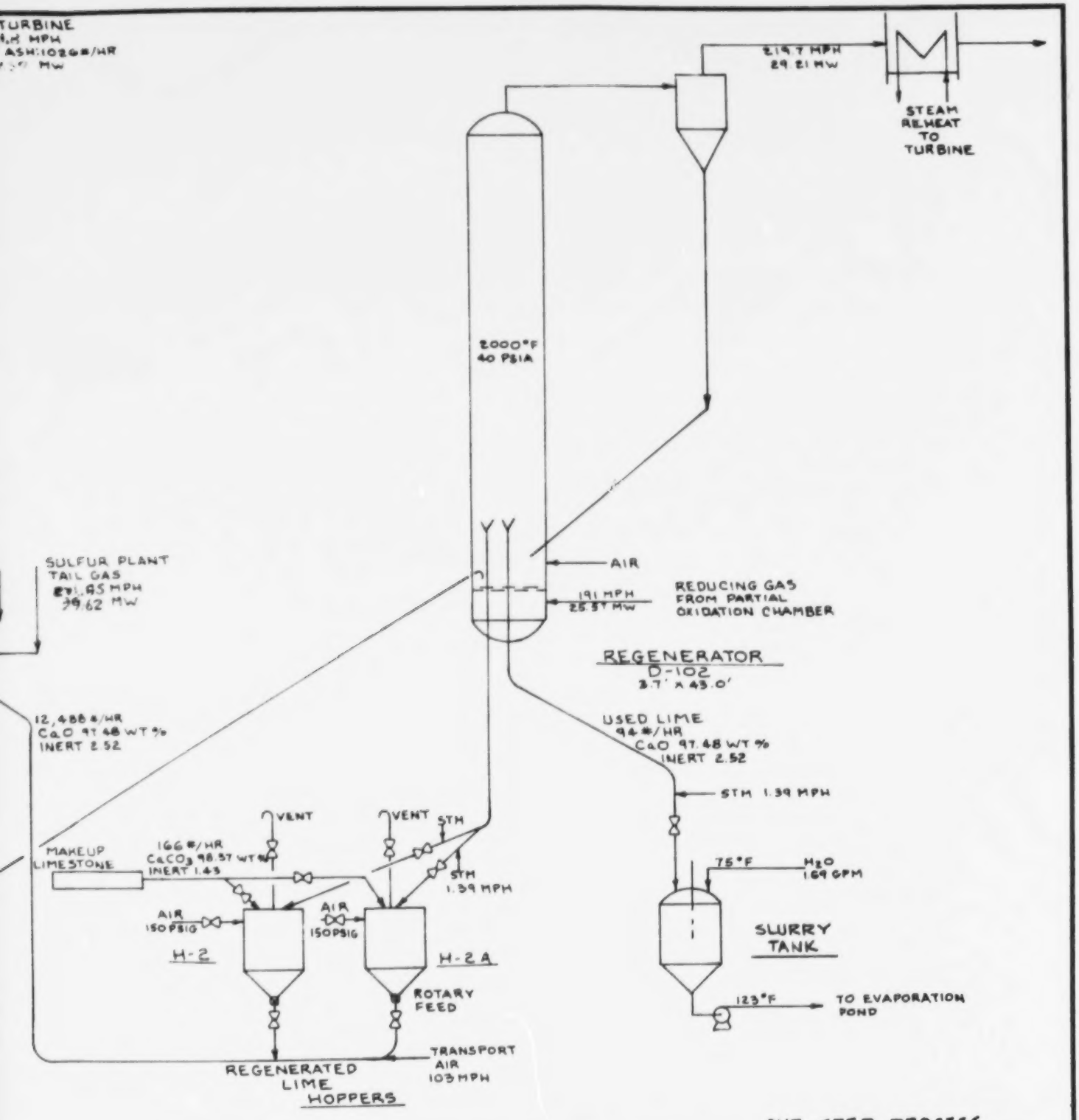


ONE STEP PROCESS

NO.	REVISION DESCRIPTION	DATE	BY	CHK.
	ISSUED FOR FABRICATION	ISSUED FOR CONSTRUCTION		

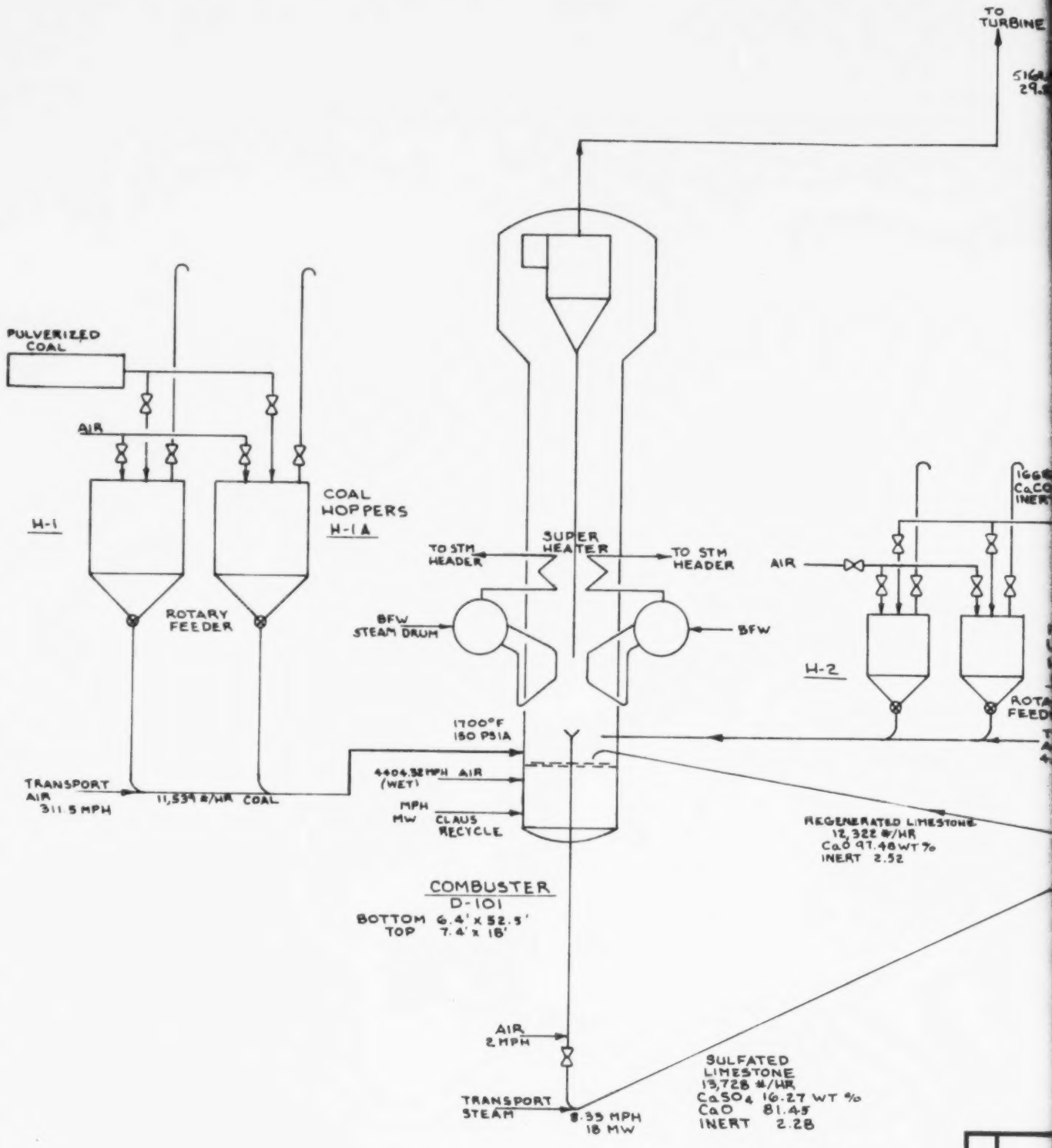
SCALE:
DRAWN:
CHECKED:
APPROVED:
DATED:

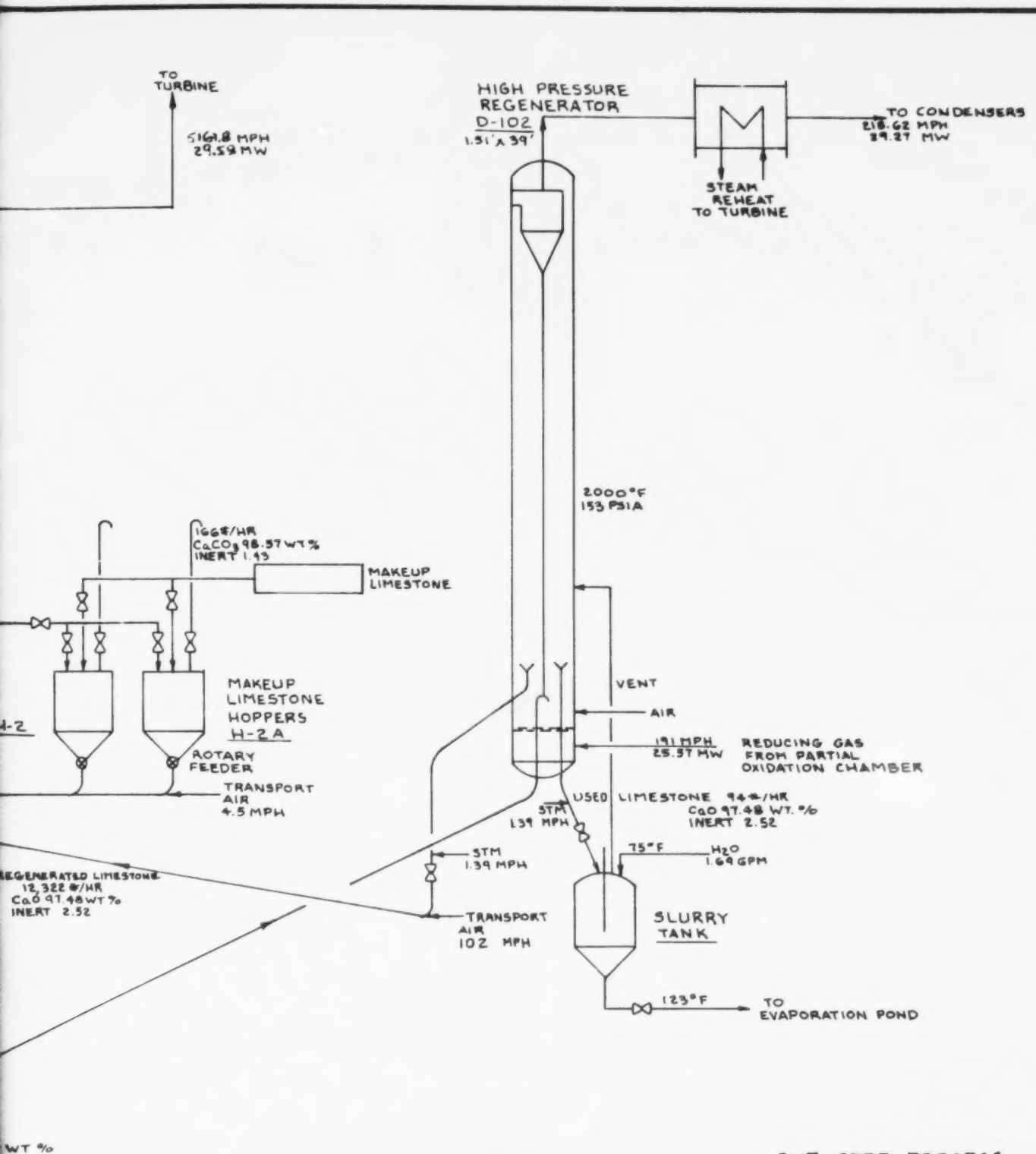
THE M. W. KELLOGG COMPANY
a division of PULLMAN INCORPORATED

FLUID BED BOILER WITH LOW PRESSURE LIME REGENERATION

CLASS	AREA	JOB NO.	DRAWING NO.
			FIG. 5

B


TO TURBINE
PULVERIZED COAL
AIR
H-1
COAL HOPPERS H-1A
ROTARY FEEDER
TO STM HEADER
SUPER HEATER
TO STM HEADER
BFW STEAM DRUM
BFW
AIR
H-2
1700°F 150 PSIA
TRANSPORT AIR 311.5 MPH
11,539 #/HR COAL
4404.3 MPH AIR (WET)
MPH MW
CLAUS RECYCLE
REGENERATED LIMESTONE 12,322 #/HR CaO 97.48 WT % INERT 2.52
COMBUSTER D-101
BOTTOM 6.4' x 52.5'
TOP 7.4' x 18'
AIR 2 MPH
TRANSPORT STEAM
8.35 MPH 18 MW
SULFATED LIMESTONE 13,728 #/HR
CaSO4 16.27 WT %
CaO 81.45
INERT 2.28



ONE STEP PROCESS

NO.	REVISION DESCRIPTION	DATE	BY	CHK.

ISSUED FOR FABRICATION | ISSUED FOR CONSTRUCTION

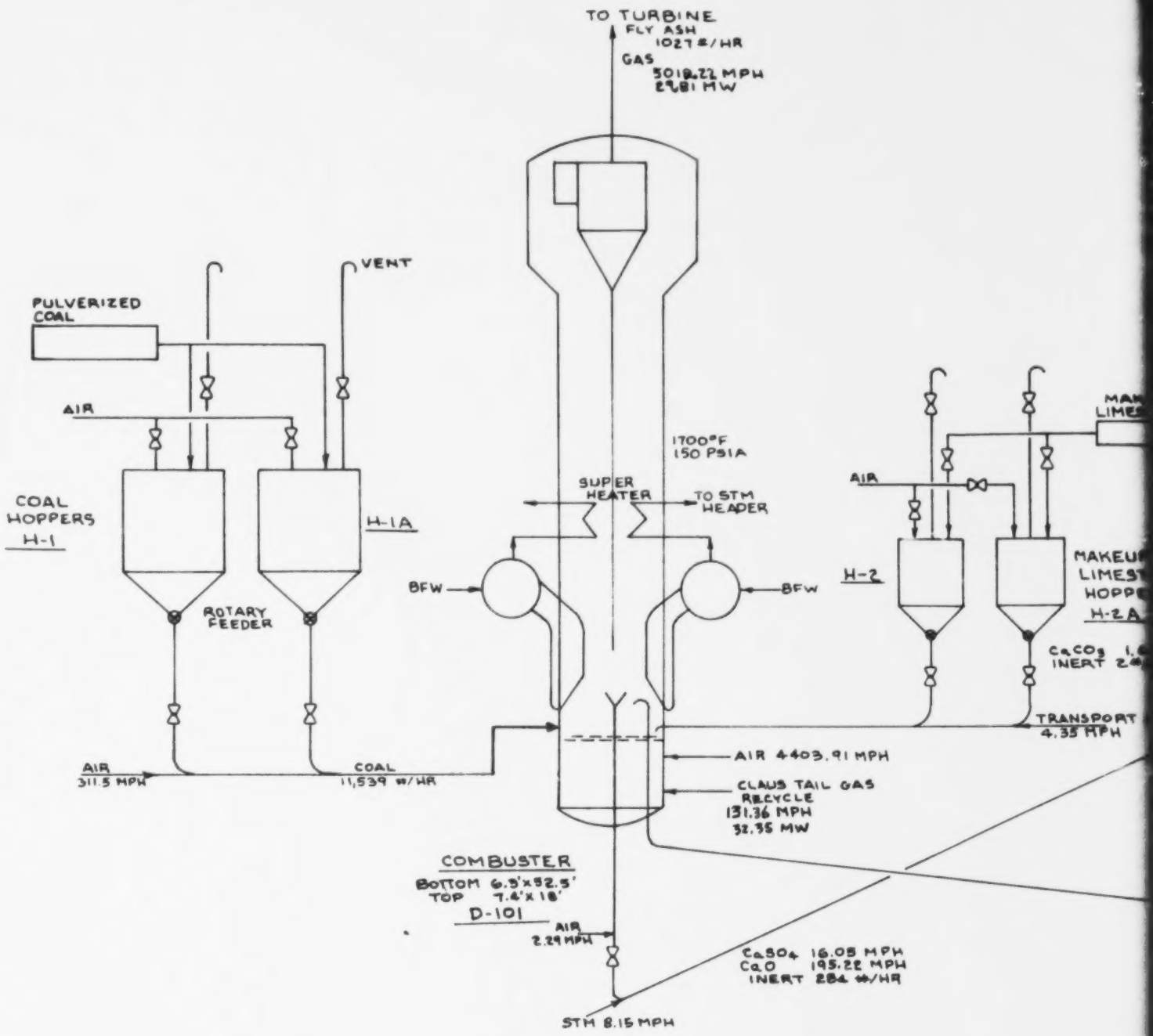
SCALE: ~
DRAWN: BCB
CHECKED:
APPROVED:
DATED:

THE M. W. KELLOGG COMPANY
a division of PULLMAN INCORPORATED

FLUID BED BOILER WITH PRESSURIZED LIMESTONE REGENERATION

CLASS	AREA	JOB NO.	DRAWING NO.
			FIG. 6

B



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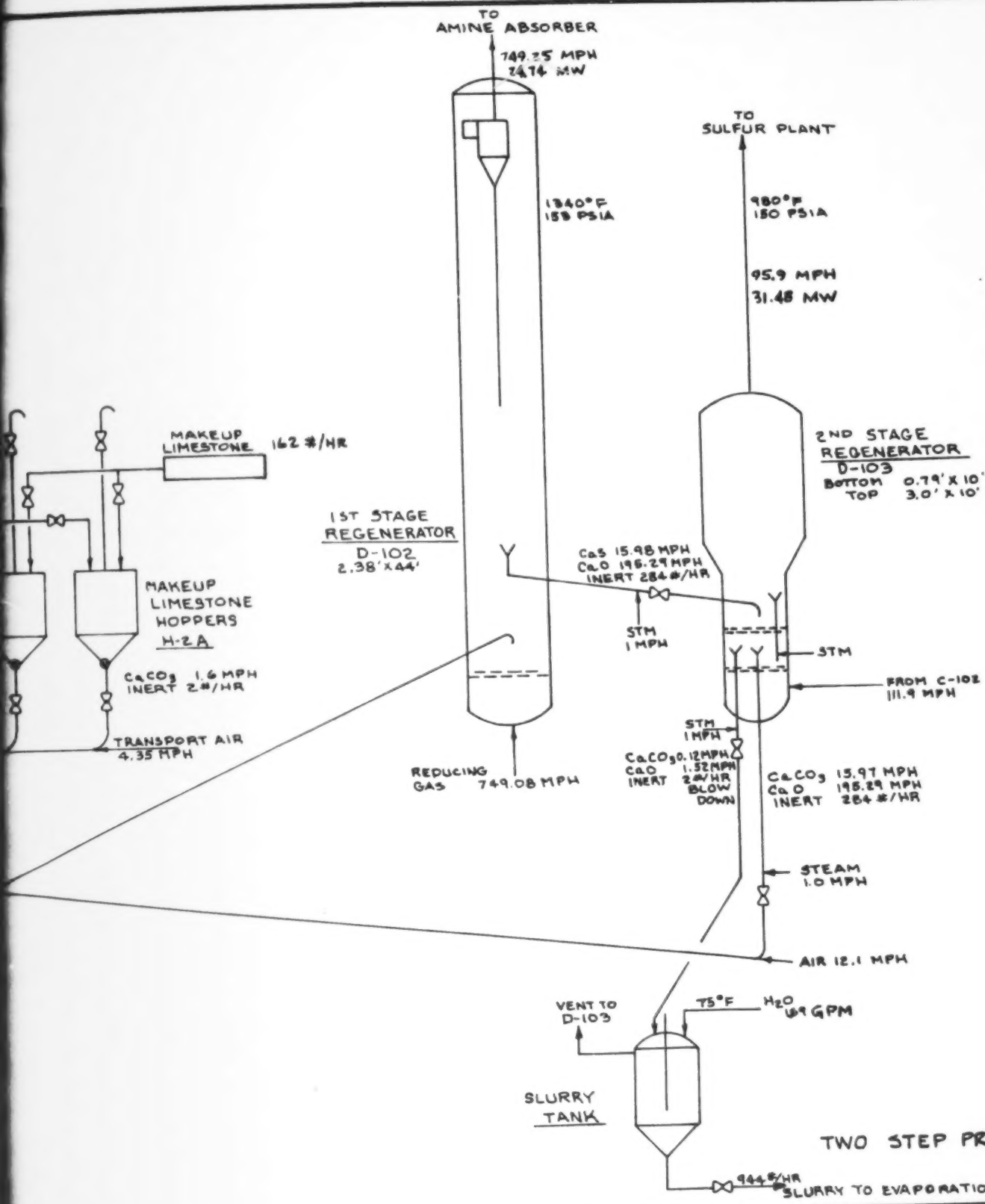

NO.	REVISION DESCRIPTION	DATE	BY	CHK.

ISSUED FOR FABRICATION | ISSUED FOR CONSTRUCTION

SCALE: ~
DRAWN: BCB
CHECKED:
APPROVED:
DATED:

THE M. W. KELLOGG COMPANY
a division of PULLMAN INCORPORATED

ALTERNATE PROCESS FOR THE RELEASE OF H_2S

CLASS	AREA	JOB NO.	DRAWING NO.
			FIG. 7

B

Appendix H

TABLE 3

COMBUSTOR HEAT BALANCE

Enthalpy Basis: 75°F

MM Btu/HR

IN		OUT	
Recycled Rock	2.020	Flue Gas*	6.192
Sulfur Plant Tail Gas	0.117	Sulfated Rock	2.290
Combustion Heat	150.000	Heat to Steam	144.100
SO_2 Absorption Heat	0.870	Heat Losses	0.425
TOTAL	153.007	TOTAL	153.007

*After being cooled in energy recovery

Appendix I

TABLE 4

Equilibrium Yields - One Step Regeneration

Temp.	:	2000°F
Press.	:	14.7 psia
$\frac{\text{Mols } (CO+H_2)}{\text{Mol } CaSO_4}$	:	1.05

Reducing Gas

Component	Mol %
CO	4.50
H_2	4.50
CO_2	6.00
H_2O	22.19
N_2	62.81
TOTAL	100.00

Product Gas

Component	Mol %
H_2	0.20
H_2O	24.38
N_2	57.86
SO_2	7.88
S_2	trace
H_2S	0.01
CO	0.15
CO_2	9.52
TOTAL	100.00

Appendix J

TABLE 5

Equilibrium Yields - Two Step Regeneration

1st Stage

Temp.	:	1340°F
Press.	:	150 psia
$\frac{\text{Mols } (CO+H_2)}{\text{Mol } CaSO_4}$	:	5.58

Reducing Gas

Component	Mol %
CO	9.00
H_2	11.50
CO_2	3.21
H_2O	21.51
N_2	54.78
TOTAL	100.00

Product Gas

Component	Mol %
CO	2.71
H_2	9.25
CO_2	9.51
H_2O	23.78
N_2	54.75
H_2S	trace
TOTAL	100.00

Appendix K

TABLE 6

Equilibrium Yields - Two Step Regeneration

2nd Stage

Temp. : 980°F

Press. : 150 psia

Inlet Gas

Component	Mol %
CO_2	50.00
H_2O	50.00
TOTAL	100.00

Product Gas

Component	Mol %
H_2S	16.54
CO_2	41.61
CO	trace
H_2O	41.64
H_2	0.21
SO_2	trace
S_2	trace
TOTAL	100.00

Appendix L

TABLE 7

Combustor & Regenerator Dimensions and Design Parameters

	Combustor	1-Step Low Pressure Regenerator	1-Step Pressurized Regenerator	2-Step 1st Stage Regenerator	2-Step 2nd Stage Regenerator
Bed Temp.: °F	1700	2000	2000	1340	980
Dilute Phase Pressure: psia	150	40	153	153	150
Superficial Velocity: ft/sec	7.0	6.0	6.0	6.0	6.0
Vessel I.D.: ft.	6.4	3.7	1.5	2.4	0.8
Expanded Section I.D.: ft.	7.4	-	-	-	3.0
Transport Disengaging Height: ft.	43.5	30.0	29.0	28.7	4.5
Entrainment at Cyclone Inlet: lb/hr	78,500				
Minimum Fluidization Velocity: ft/sec	2.4	2.6	2.4	2.4	2.4
Sluffing Height: ft.	17.0	9.85	4.0	6.3	2.1
Overall Height: ft.	70	43	39	44	20

Appendix M

Reduction of $CaSO_4$-Summary of Literature Search

1. General Literature Review

a. Comments on Review of Literature

Since the literature search did not find any directly pertinent information on the reduction of $CaSO_4$ or $CaSO_4 \cdot MgO$ under pressure, the literature and experience at atmospheric pressure (1,2)* must be used to analyze the problems which may occur under pressure.

An Esso patent, U.S. 2,970,893 (6) is completely lacking in detailed experimental information. Pressures noted are atmospheric to 1000 psig (claim 3) and the statement is made that 10 to 200 psig may be used advantageously in fluidized bed operation. In essence, gypsum is converted to lime by reduction with methane-steam at 850-1500°F (no O_2), preferably 1200-1400°F, using cobalt molybdate on alumina catalyst and an excess of theoretical methane and steam. Ratio of $CaSO_4$ to catalyst is between 1 to 1 and 10 to 1, and steam to methane (or hydrocarbon) must exceed the theoretical requirement. Novel (if true) is the use of solid catalyst with gypsum to lower the temperature of reaction and the liberation of hydrogen sulfide rather than sulfur dioxide.

Wheelock's thesis (1) has a good review of the literature to 1958 on $CaSO_4$ decomposition and reduction (pp.21-29). Carbon monoxide starts to react at 1300°F but the rate increases rapidly with temperature up to 1650°F (maximum temperature investigated). The reaction is:

$$CaSO_4 + 4CO \rightarrow CaS + 4CO_2$$

Using dry and wet hydrogen led to some H_2S in the exit gas. One author (Riesenfeld-7) studied the action of dry and wet methane. At 1470 to 1830°F dry methane quantitatively reduced $CaSO_4$ according to the reaction:

$$CaSO_4 + CH_4 \rightarrow CaS + CO_2 + 2H_2O$$

*Numbers in () refer to references listed at the end of this section.

With water present, gypsum was completely converted into calcium oxide and sulfur dioxide, given sufficient time, by using a large ratio of water to methane and a temperature of 2200°F or higher.

Zawadzki (3) found dry H_2 reduced $CaSO_4$ to CaS quantitatively at a temperature range of 1110-1470°F. Above 1470°F it was noted that CaO formed and at 1920°F it predominated. Sulfur came off as SO_2 and free S. He found CO did about the same thing but the rate was not as rapid. In 1956, Burwell patented a process (U.S. 2,740,691) for converting finely divided gypsum to lime and hydrogen sulfide by reduction with hydrocarbon gas and steam at a temperature range of 1630 to 1830°F. He apparently used a large excess of steam (8).

The following reaction is of interest because it is involved in some of the previous observations:

$$3CaSO_4 + CaS \rightleftharpoons 4CaO + 4SO_2$$

The literature indicates that this reaction occurs at 1830°F and higher. The following reaction has been shown to occur:

$$CaS + H_2O \rightarrow CaO + H_2S$$

However the equilibrium constants indicate it would not be practical (1, p. 29).

In reviewing this and other literature, an exact equation illustrating the reaction of calcium sulfate, methane and steam has not been found. The following equation can be written assuming the products shown:

$$CaSO_4 + 2CH_4 + H_2O \rightarrow CaO + H_2S + 2CO_2 + 4H_2$$

Excess steam would decrease the CO concentration. As is evident from the equation, 3 volumes of gas are changing to 7 volumes; this is definitely in the direction where pressure is working against the reaction. The work of Wheelock(1) shows that by keeping the concentration of CO and H_2 low, the formation of lime instead of calcium sulfide predominates at high temperatures.

Depending on temperature, the CO_2 and H_2 may react and reach water gas equilibrium:

$$CO_2 + H_2 \rightarrow CO + H_2O$$

The cobalt molybdate catalyst, a hydrocarbon desulfurization catalyst, is stated in the Esso patent(6) to lower the temperature for the $CaSO_4$, CH_4, H_2O reaction. It may be that the cobalt molybdate catalyst does some steam reforming; namely, it catalyzes the formation of hydrogen and carbon monoxide:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

The CO and H_2 formed then reduce the calcium sulfate at temperatures below 1500°F to calcium sulfide:

$$CaSO_4 + CO + 3H_2 \rightarrow CaS + CO_2 + 3H_2O$$

The use of excess steam helps to convert some of the CaS to calcium oxide and hydrogen sulfide:

$$CaS + H_2O \rightarrow CaO + H_2S$$

Although the equilibrium constants show this reaction is unfavorable, it may occur to some extent by keeping the pressure of hydrogen sulfide low with excess steam. The cobalt molybdate catalyst may catalyze the following reaction as well:

$$CaS + 3H_2 + CO \rightarrow CaO + H_2S + CH_4$$

The catalyst may aid in the removal of sulfur as hydrogen sulfide by some mechanism which operates as it does in desulfurization of organic compounds. Pressure would be favorable here to diminish carbon formation on the catalyst (coke on catalyst gets hydrogenated to methane).

The memorandum of February 25, 1971 by E.L. Plyler of EPA indicates Esso RED is using 1900-2000°F in a fluidized bed combustor to regenerate lime and produce sulfur dioxide. At this temperature the following reaction becomes significant:

$$3CaSO_4 + CaS \rightarrow 4CaO + 4SO_2$$

This is a considerable temperature departure from the Esso patent. Wheelock's equilibrium constants for this reaction are (p. 33):

Temperature: °F	$\log_{10}K$	$\Delta H°$: Kcal/gram-mole
1700	-4.67	240
2060	0.96	211
2420	4.95	198

Thus temperatures above 1800°F are needed and the heat duty is high. Other literature is cited in reference (2). None of this was done too critically and it adds little to the survey.

If Esso is doing what is indicated by Plyler's memorandum and is still using methane and steam, then another equation must be written, namely:

$$CaSO_4 + CH_4 + H_2O \rightarrow CaO + SO_2 + CO_2 + 3H_2$$

The high temperature also would favor the gas phase reaction:

$$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O$$

Plyler's memorandum indicates SO_2 is the product and not H_2S; thus it is concluded that methane and steam probably are not the reactants. The combined reaction is shown below:

$$CaSO_4 + CH_4 \rightarrow CaO + CO_2 + H_2S + H_2O$$

The effect of pressure is unfavorable since three gaseous volumes are obtained from one gaseous volume.

b. Pertinent Information in June 14, 1971 Memorandum of EPA-OAP

On page 3 of this memorandum, reference is made that Esso has shown high SO_2 removal rates from a flue gas by using a fluidized bed reactor at about 1600°F and a gas velocity of 6 fps. The use of limestone as the fluidized bed material and its regenerability have been demonstrated. On page 4, a two-stage FBC unit burned a high sulfur residual oil (Esso Res., Ltd.). Continuous regeneration of limestone and recovery of sulfur values is part of this Esso concept. These British Esso workers mentioned five problems:

1. Metal erosion in the fluid bed
2. Carbon loss by solids carryover
3. Distribution of coal and air uniformly
4. "Turndown" capability of bed
5. Control of steam temperature and pressure over range of boiler conditions.

Effort by OAP is concentrating on regeneration of limestone sorbent beds for combustors and gasifiers, both atmospheric and pressurized, for coal and oil.

Esso RED has evaluated the combustion of finely ground coal in a fluidized bed of coarse limestone. They explored the regenerability of the limestone. They are seeking a method of reducing NO_x and SO_x emissions by interaction between NO_x and SO_x. They are designing a 12" ID continuous pressurized FBC using regenerable limestone.

As Zielke et al (4) point out, MgO in the dolomite derived product has no ability for SO_2 absorption due to equilibrium limitations. After regeneration the most probable form will be the oxide.

What will be the composition of the sulfated limestone or dolomite from the combustor-absorber? Zielke (4) shows that in 7 cycles the dolomite went from 77% to 28% efficiency of sulfation, i.e. $(CaSO_4 \times 100)/(CaO + CaSO_4)$. They used a regeneration temperature of 1950°F which is high enough to cause sintering which may account for the loss of efficiency during cycling.

If Esso intends to employ cobalt molybdate desulfurization catalyst and allows much lower regeneration temperatures as indicated by the patent, then the efficiency could be maintained at a much higher level. Economic evaluation should be brought in here to determine the justification for use of the catalyst. Other difficulties are apparent as well. Since the SO_2 acceptor is coarse, what size should the catalyst be? Work is necessary to allow adequate separation of catalyst from the lime-containing product. The Esso patent requires carbon burnoff from the cobalt molybdate catalyst. In addition, at 1400°F the cobalt in the desulfurization catalyst may react irreversibly with the alumina to form a cobalt aluminate which could be inactive; thus the catalyst could lose activity as well.

c. Problems in Regeneration of Limestone

Many assumptions will be made in the following in view of the lack of knowledge and data on the pressurized regeneration of the sulfated limestone. First, it is assumed that a superficial gas velocity of about 5-10 fps will be used; this will fix the limestone size on the coarse side. Wheelock(1) used 7/8 mesh and Zielke et al (4) used a dolomite of 14/35 Tyler mesh.

The limestone or dolomite to use can be answered in part by the Consolidation Coal Company which has done a large amount of evaluation of these substances for use in their coal gasification process. The fact that they used one of the best attrition resistant dolomites in their work (4), namely a Tymochtee dolomite from Western Ohio, is a good start. A program on easily obtained limestones in plentiful supply may involve a study of strength and attrition rates before activity evaluation. No doubt many of these studies have been done already.

The use of the word limestone means calcium carbonate and dolomite means calcium magnesium carbonate. However, the experimental conditions of temperature and carbon dioxide pressure will determine whether the limestone remains as such or is converted to lime in use and whether the dolomite is converted to $CaO \cdot MgO$.

The obvious advantages of pressure to reduce equipment size, etc., may outweigh any negative mass action effect and may even improve kinetics through concentration effects, compositional changes (CaO to $CaCO_3$, etc.) and a change in mechanism.

Attrition rates of catalyst and limestone must be low enough to be economical.

In summary, lack of exact knowledge concerning the method of regeneration has limited this discussion. It does appear that high temperature atmospheric processes (above 1800°F) give good rates of reaction and have established feasibility. Pressure may have little effect except for some of the reasons noted. Below 1800°F, e.g., 1200 to 1500°F, if a catalyst such as cobalt molybdate is used, it is important that it maintain its activity. Much laboratory scale experimentation can be done to answer many of these questions. In this latter temperature region, the use of coarse sulfated lime may be a deterrent to reasonable efficiencies as well as reascnable absorption rates.

2. Specific Literature Review

Since A.M. Squires is well known for his work in this area the recent literature has been searched for his publications (5). Not all papers were obtained, but probably a sufficient number have been found to complete this investigation. The CCNYU library was contacted concerning the reference of Narayanan. They stated they had nothing as he was not in the graduating class of 1970 or 1971. However, in a recent publication (JAPCA for May 1971), his name appears in the acknowledgement as having performed experimental work for Squires and he may not have graduated as yet. In summation of this review, no direct experimental work is available to define the kinetics for pressure reduction of calcium sulfate.

In reviewing Squires' work from 1966 to now, a pattern appears: (1) the early work was concerned with utilization of fully calcined dolomite to absorb H_2S, and then the main theme of Squires was used to liberate H_2S by reaction of the formed CaS with steam and CO_2 followed by calcination of the $CaCO_3 \cdot MgO$ to $CaO \cdot MgO$ for reuse; (2) the recent trend is to absorb SO_2 with half calcined dolomite, (i.e., $CaCO_3 \cdot MgO$), reduce the $CaSO_4$ to CaS with H_2 + CO from a steam methane

reformer, liberate H_2S as before and return the half calcined dolomite for reuse. The early publications assumed fuel desulfurization under gasification-type conditions where H_2S would be the sulfur compound available for reaction with the calcined dolomite. The later publications recognize that SO_2 may be liberated during combustion or partial combustion and a panel bed filter with half-calcined dolomite is proposed for SO_2 scrubbing of the flue gas.

The 1967 paper (Paper No. 1) by Squires presents the original concept with relevant thermodynamics and chemistry and only a minor amount of feasibility type experimental data. It is a lengthy paper in which he proposes the use of calcined dolomite to abstract sulfur from the fuel (9):

$$H_2S + CaO \cdot MgO \rightarrow CaS \cdot MgO + H_2O \qquad (1)$$

Then Squires' main theme, the liberation of H_2S by steam plus carbon dioxide follows:

$$CaS \cdot MgO + H_2O + CO_2 \rightarrow CaCO_3 \cdot MgO + H_2S \qquad (2)$$

The regeneration of the calcined dolomite is the next reaction:

$$CaCO_3 \cdot MgO + \text{heat} \rightarrow CaO \cdot MgO + CO_2 \qquad (3)$$

Feasibility of reaction (2) was established at 1000°F and 220 psia. An inlet gas with a composition of 82% CO_2, 9% H_2, and 9% CO was blended with steam to give a CO_2/H_2O ratio of 1.75 which yielded a dry gas of 20-24% H_2S (about equilibrium). Feasibility for reactions (1) and (3) was also established. Squires did state kinetics are needed for process development.

Squires, soon after the above papers were given (September, 1966), became a professor at CCNYU where he has been working to obtain the kinetic data and to further develop this and other concepts. Although a copy of the series paper (Abstract

labeled No.1) was not obtained, the second paper (No. 2) includes additional kinetic data on the CaO plus H_2S reaction (1). Actually, the use of half-calcined dolomite as well as fully calcined is now considered.

$$CaO \cdot MgO + H_2S \rightarrow CaS \cdot MgO + H_2O \qquad (1)$$

$$CaCO_3 \cdot MgO + H_2S \rightarrow CaS \cdot MgO + H_2O + CO_2 \qquad (4)$$

Release of H_2S is still obtained with CO_2 and steam at a temperature of 1200°F or lower by the reversal of reaction (4).

In this article, Squires goes into considerable kinetic detail to rationalize the rate data and make a model. He also points out the importance of the freshly calcined material and cautions that more work is needed for application of the data. Noted is the lack of data under steady state process conditions. This work only represents a beginning. So far Squires requires that the sulfur be freed from the fuel as H_2S in order to react with the fully or half calcined dolomite.

In Abstract No. 3 mention is made of capturing sulfur, either as SO_2 or H_2S, with fully or half calcined dolomite. This is the first notation by Squires of a combustion reactor rather than gasification or carbonization only. To use the H_2O+CO_2 liberation of H_2S from CaS, then any $CaSO_4$ formed must be reduced to CaS before treatment.

Another article (Paper No. 3) by Squires which may be of general interest is from Chemical Engineering and is entitled "Keeping Sulfur Out of the Stack". On page 186 he indicates his high pressure process of recovering H_2S (for a Claus plant) is probably the best way to go.

In the paper labeled No. 4, only the first page was copied as it mainly is a mathematics paper and not extremely pertinent. However, it does indicate Squires' new concern with scrubbing the flue gases for removal of fly ash and SO_2 and the use of panel filters which is also mentioned in Abstract No. 2. The last paper (labeled No. 5) contains most of the experimental information generated at CCNYU (Note that Squires is now Chairman of the Chemical Engineering Department at CCNYU). However, this paper is concerned with scrubbing stack gas from power stations.

The stack gas process scheme considers converting dolomite at 1300°F with 25% CO_2 in N_2 to half-calcined dolomite, $CaCO_3 \cdot MgO$, which is used in a panel bed filter at about 1100°F to absorb SO_2 from the flue gas and yields $CaSO_4 \cdot MgO$ (10). The spent sulfated dolomite is reduced with H_2+CO (ex CH_4-H_2O) at about 1400°F with 25% H_2O, 25% H_2, 25% CO, 25% CO_2 to produce $CaS \cdot MgO$ and unconverted $CaCO_3 \cdot MgO$. Treatment with H_2O+CO_2 at 1200°F under pressure springs out the H_2S and regenerates the $CaCO_3 \cdot MgO$ for reuse.

The results of J.R. Coke (11) were confirmed by Esso and by Squires on the reactivity of half calcined dolomite with SO_2 at 1100°F, i.e.:

$$CaCO_3 \cdot MgO + SO_2 + 1/2O_2 \rightarrow CaSO_4 \cdot MgO + CO_2.$$

Coke, in fact, using a fixed bed of usually 1/8 x 1/4 inch dolomite did a fair job of investigating the variables and arrived at a kinetic expression. Squires found the kinetic expression did not satisfy his smaller size dolomite, 10/28 mesh. Coke's results usually showed about 50% conversion whereas Squires obtained 50 to 90% conversion depending on size. However, in a panel bed filter Squires assumes 8/40 mesh stone and 50% conversion for calculation. Thus 100 lbs of $CaCO_3 \cdot MgO$ could take up 22.8 lbs SO_2 (comparable to Bureau of Mines alkalized alumina). Squires also indicates space

velocities in the panel bed filter which seem quite low.

Lack of data on reduction of the sulfated limestone ($CaSO_4 \cdot MgO$) still is evident. Thus, nothing further can be added to what has been said before. The concepts of Squires seem to be quite good, but supporting process information is lacking. The M.W. Kellogg molten salt work substantiates the liberation of H_2S by $H_2O + CO_2$ treatment of sulfides. Reaction rates are needed though. The pressure effect in most of Squires' reactions should be advantageous.

(1) Wheelock, T.D., Ph.D. Thesis, "Desulfurization of Gypsum," Iowa State College (1958), University Microfilms L.C. Mic 59-1152.

(2) "Sulfur from Gypsum," Scientific Information Association, Literature Review. Temple, Texas (1967).

(3) Zawadzki, J., Konarzewski, J., Lichtenstein, W.J., Szymankiewicz, S., and Wachsztejnski, J., Roczniki Chem. 6: 236-255, 1926.

(4) Zielke, C.W., Lebowitz, H.E., Struck, R.T., Gorin, E.J., "Sulfur Removal During Combustion of Solid Fuels in a Fluidized Bed of Dolomite", Air Pollution Control Association, 20, 164/1970.

(5) Pell, M., Graff, R.A., Squires, A.M., Desulfurization of Fuels with Calcined Dolomite; II Reaction of CaO with H_2S., CEP Tech Manual, "Sulfur and SO_2 Development" (1971).

(6) Viles, P.S., "Production of Lime and Hydrogen Sulfide", U.S. Patent 2,970,893, Esso Research and Engineering Company, February 7, 1961.

(7) Riesenfield, E.H., Journal of Prakt. Chem., 100: pp. 115-158, 1920.

(8) Burwell, A.L., "Process for the Recovery of Lime and Hydrogen Sulfide from Calcium Sulfate", U.S. Patent 2,740,691, April 3, 1956.

(9) Squires, A.M., Graff, R.A., Pell, M., "Desulfurization of Fuels with Calcined Dolomite; I. Introduction and First Kinetic Results", CEP Symposium Series, No.115, Vol. 67, pp. 23-34.

(10) Squires, A.M., Graff, R.A., "Panel Bed Filters for Simultaneous Removal of Fly Ash and Sulfur Dioxide; II. Reaction of Sulfur Dioxide with Half-Calcined Dolomite", Journal of Air Pollution Control Association, Vol, 21 (5), pp. 272-276, May 1971.

(11) Cokes, J.R., "The Removal of Sulfur Oxides from Waste Gases by a Dry Method", Doctoral Thesis, University of Sheffield, England, May, 1960.